VIII. *Researches on the Action of Organic Substances on the Ultra-violet Rays of the Spectrum.*

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[Plates 21–34.]

PART I.

Method of Experimenting.—Examination of Alcohols and Fatty Acids.

In the year 1863 the late Dr. W. A. Miller described his method of examining the diactinic properties of various saline solutions and organic substances. (Miller, "On the Photographic Transparency of Various Bodies, &c.," Phil. Trans., 1863, I.)

He found that the spectrum transmitted by lenses and prisms of rock-crystal was far superior in length as determined by sensitive photographic plates, to that obtained when lenses and prisms of glass and other materials were employed. He found particularly that the spectrum produced by passing electric sparks between silver points was very rich in photographic rays, and he ascertained how far various substances were transparent to these rays. Professor Stokes at the same time communicated results he had obtained when studying the long spectrum of the electric light by receiving the rays on a fluorescent screen. (Stokes, "On the Long Spectrum of Electric Light," Phil. Trans., 1863, I.) He discovered the fact that certain solutions showed light and dark bands which were otherwise invisible. More recently, M. Soret has studied the absorption of the ultra-violet rays of the spectrum transmitted by various substances, using for the purpose a spectroscope of his invention, which has a fluorescent eye-piece. (Soret, "Recherches sur l'Absorption des Rayons Ultra-violets par diverses substances," 'Archives des Sciences Physiques et Naturelles;' Geneva, January, 1878.) In 1872 the apparatus of Dr. Miller was reconstructed by one of us, and certain improvements were introduced. The intention of repeating his experiments and carrying them out in a more complete manner was prompted by a desire to know what relation, if any, exists between the molecular constitution and the actinic absorption of organic substances. No encouragement to pursue this line of research was offered by the results of Dr. Miller, since he states, "I have not been

able to trace any special connexion between the chemical complexity of a substance and its diactinic power." ('Journal of the Chemical Society,' vol. ii., p. 68.) Thus water was found to be perfectly diactinic, and ethylic alcohol more than methylic alcohol, though less so than water. Since all the physical properties of organic substances are dependent on their molecular constitution, it is very probable that the photographic transparency of a substance is a delicate test of its purity, and that notwithstanding the care taken in the purification of specimens, yet some of the experiments of Dr. MILLER were made with impure substances. In the face of this difficulty it was thought that by observing a large number of bodies of similar constitution, many of which would be metameric substances, such as the ethereal salts of the organic acids, and homologous series of the normal alcohols and acids, evidence might be forthcoming of the influence of impurities, and the variations in the absorption of the invisible rays caused by each increment of CH_2 in the molecule. As according to the researches of MILLER the physical state of a substance does not generally affect its absorptive power, we may avoid the difficulty of making observations on equal volumes of organic substances in a state of vapour, and easily arrive at the maximum absorption due to a molecule of a substance, by taking into account its specific volume in the liquid state, and by making the thickness of the layer of liquid experimented on proportional to its specific volume, or by dissolving molecular weights of substances in solvents of known transparency.

The Method of Experimenting.

After considerable time spent in giving a trial to the various methods of studying the ultra-violet rays, the photographic method appeared to be decidedly the most satisfactory.

Rays which are very indistinct, or even quite invisible on any fluorescent screen, may be brought out distinctly on a properly prepared photographic plate. It is useful, however, to have a focussing screen of uranium glass in the camera, or what answers the purpose equally well, a glass plate coated with gelatine in the solution of which some æsculin has been dissolved. To observe the spectrum by reflected light, and view the visible and invisible rays simultaneously, a piece of paper steeped in a solution of æsculin, to which a little ammonia has been added, may be employed, and it answers the purpose even when dry.

The instruments employed were the following:—1st. An induction coil and Leyden jar for producing an unbroken stream of sparks between metal points. 2nd. A collimator tube 3 feet long, carrying a pair of clips at one end for holding the points close to the slit, and a quartz lens at the other. 3rd. A quartz prism placed at the angle of minimum deviation for the sodium line D. 4th. Another quartz lens and the body of a photographic camera which could be extended to 36 inches. The separate portions of this lengthy apparatus were firmly screwed down to two heavy tables to prevent the shifting of any part, since the proper adjustment of the whole takes some

time. The coil, which could give a 6 or 7-inch spark in air, was excited by a battery of five GROVE'S cells. Other batteries were tried, but none gave such satisfactory results when working for hours together. The Leyden jar was of such a size that each surface of tinfoil measured 72 square inches.

The carriers for the metallic points are so fixed to the collimator tube that by the motion of two screws they may be moved from right to left across the slit, and at the same time as close as desirable under different circumstances. The proper position of the carrier is, of course, a vertical one, but it could be turned over in a horizontal direction so as to afford convenience for fixing the points. The electrodes are more conveniently held by screw forceps than by spring clips. Broad electrodes, as former experimenters have pointed out, are usually the best to work with (MILLER and STOKES, *loc. cit.*), but we have in certain cases obtained better results with points, as for instance, with nickel wire. The spark apparatus was enclosed in a wooden box along with the end of the collimator tube to prevent the light emitted by the electrodes from escaping into the dark room, and to muffle the irritating noise of the electric discharge. We have had no difficulty in obtaining an uninterrupted stream of sparks yielding a perfectly steady light for three quarters of an hour. Professor STOKES used a condensing lens of $2\frac{1}{2}$ inches focal length to concentrate the rays of the spark upon the slit, but since we sometimes employed an amalgam containing several metals as the lower electrode, we could not use the same, for the reason that mercury vapour would condense upon the lens. Instead of condensing the rays with a lens, we diminished the loss of light very greatly by fixing the electrodes as near as possible to the slit, and placing the cell holding the liquid to be examined in a little wooden box behind the slit, into which the collimator tube passed. This box was about 4 inches long, with a hinged lid, and it was possible to place a train of three or four cells full of liquid within it, through which the rays were transmitted.

The cells themselves were cut from wide glass tube by slicing it longitudinally in two pieces and cutting off lengths of three-quarters of an inch. These were fitted in metal frames, and pieces of quartz were affixed to each end by means of screws pressing upon a rim of metal. The situation of the liquid behind the slit, and therefore at a distance from the spark, obviated a difficulty caused by the ignition of the vapour of volatile liquids. The tube of the collimator, however, became filled with vapour, which of itself would exert a strong absorption in many cases, and in order to remove this vapour a nozzle was fixed at right angles to the tube at a point as close to the lens as possible, and this was placed in communication with a concertina aspirator, two or three strokes of which will draw five or six litres of air through the tube.

The lens behind the prism was capable of being raised and lowered by means of a sliding front as on an ordinary landscape camera. This enabled us, when occasion required, to take three photographs on a plate 2 inches in width. According as was found most convenient we have made use of electrodes of silver, cadmium, zinc, aluminium, nickel (containing as we find by its spectrum a trace of copper), indium,

and iron. In some cases an amalgam containing silver, zinc, cadmium, sodium, aluminium, and magnesium has been used together with a point of iron. The spectrum most generally useful is that yielded by nickel points. In certain cases, particularly when several absorption bands occur, it is advisable to photograph with the slit open, so that the nickel lines may not be too distinct.

The Photographic Process.

The original method of photographing employed by Dr. MILLER we have found to be defective: first, because the more refrangible end of the ultra-violet spectrum is extremely weak, if not entirely wanting, when photographed on plates containing a plain iodised collodion; secondly, a wet collodion process is disadvantageous when long exposure is sometimes necessary; and thirdly, when working in a small room the ozone generated by the electric discharge acts upon wet collodion plates in such a manner that they become coated with a thick deposit of silver directly the developing solution is applied, the deposit being densest where the bath solution has most accumulated. Much larger and better spectra are obtained by using ordinary bromo-iodised collodion and an iron developer, but of course this process is rendered useless by the action of the ozone on the silver solution.

The extraordinary improvements made of late years in the preparation and development of dry plates, together with the foregoing facts, combined to recommend a dry process.

Successive trials have been made with plates coated with washed collodio-bromide emulsion, with the BEECHY standard dry plates, uranium plates, Mr. KENNETT'S and WRATTEN and WAINWRIGHT'S gelatine pellicle plates. The gelatine plates are to be preferred for two reasons; if they are wanted for the production of negatives to print from, the film is exceedingly fine and even in texture, and on the other hand, if transparencies showing absorption bands are desired they need not be varnished. The BEECHY plates are more sensitive to very feeble rays in a certain part of the spectrum than those coated with gelatine pellicle; this may be seen by comparing the spectra of iron photographed on these two varieties of plates. One advantage of the gelatine plates is that they photograph more of the less refrangible rays than any others we have tried, and though the lengthening of the spectrum in consequence is comparatively slight, yet it is of importance in the examination of certain coloured substances, which while they transmit rays of higher refrangibility absorb the blue and violet. Such bodies are solutions of the nitrophenols and nitranilines. The exposure of the sensitive plates has been varied from 10 seconds to an hour and a-half, according to circumstances, depending partly on the plates employed and the object to be attained; but it is seldom that a longer period than a minute is necessary even for the production of negatives to print from, and when photographing absorption spectra with an open slit 10 seconds will suffice.

The Measurement of Bands and their Position.

The lines of zinc, cadmium, and aluminium offer a convenient means of determining the position of absorption bands, &c., and M. SORET has employed them. The lines of cadmium in the ultra-violet as well as in the visible portion of the spectrum have been measured by M. MASCART and their wave-lengths calculated. M. SARASIN has made use of these measurements in his determination of the refraction indices of quartz for the ordinary and extraordinary rays in the ultra-violet spectrum. ('Archives des Sciences Physiques et Naturelles;' Geneva, vol. lxi, p. 109; January, 1878.) The wave-lengths for the cadmium lines in the invisible portions of the spectrum are shown in Diagram No. 1, and it will be seen that several of the following diagrams have been made after this scale, it being an advantage to have the metallic lines placed at intervals corresponding to their wave-lengths. When nickel points instead of cadmium have been used, two strongly marked air-lines below the solar line L (Plate 21, fig. 1) serve as a starting point for measurements; another air-line between the lines 11 and 12 also answers the same purpose. Inasmuch, however, as the appearance of spectra as seen when photographed is different from that when the lines have been mapped out in accordance with their wave-lengths, it has been considered desirable to follow the plan of M. SORET and lay down the spectra in some cases just as they appear in the photographs.

Some of the advantages derived from the employment of photography in studying the ultra-violet rays are the following: The measurements are free from any personal error, the photographs are permanent and unmistakable records easily referred to, and the observations are made more rapidly and with much less fatigue to the eye than by any other means. Furthermore, liquids which are slightly turbid and unfit for observation with a fluorescent screen or eye-piece can be examined photographically by lengthening the exposure of the plate.

Absorption Caused by Films of Canada Balsam.

It was considered very desirable to know whether Canada balsam, as used in the construction of optical apparatus, was capable of cutting off the ultra-violet rays to any considerable extent. We are aware, from the researches of M. SORET, that Iceland spar is extremely transparent, the 26th line of cadmium being distinguishable through a thickness of 65 m.m. of the substance. It was only necessary, then, to take a small NICOL'S prism and interpose it between the slit and the first lens. The result showed that lenses and prisms, cemented with Canada balsam, are utterly useless for such experiments as these, the more refrangible rays being cut off sharply at the 12th line. Several kinds of beautifully clear and colourless optical glass, made by FEIL, of Paris, and lent us by Mr. HILGER, have the same effect upon the spectrum, whether the glasses be made of lead or aluminium; they are all utterly valueless for observations on rays more refrangible than line No. 12 of cadmium. Fluor spar is quite transparent.

Examination of Organic Substances.

After making a preliminary series of observations on the alcohols, ethereal salts, and fatty acids, we abandoned the use of silver electrodes used by Dr. MILLER, and at once, by the aid of other metallic spectra (referred to on diagram No. 1), investigated the comparative transparency of quartz in use for constructing cells, the cells being filled with water and with different alcohols.

It will be seen that the sides of three quartz cells are almost quite transparent, and that, when filled with water, they are practically unchanged in this respect.

It is evident that we need not fear to employ the three cells in a train, or to use pure water as a solvent for such substances as we may desire to examine in solution. The thickness of liquid examined was never less than three-quarters of an inch.

Many of the following organic substances were obtained from Mr. KAHLBAUM'S agents; they were prepared in his factory, and were afterwards carefully rectified and purified by us.

Methylic Alcohol. Specimen No. 1.—This was apparently perfectly pure; it had no odour or colour, and it boiled at 66° C. It transmitted very few rays beyond 12 Cd, and it is worthy of remark that, both before and after distillation from quick-lime prepared from pure marble, it yielded the same absorption spectrum. The identical specimen of methylic alcohol examined by Dr. MILLER was compared with this, and was found to give the same spectrum. The bottle containing it was labelled "Methylic alcohol from methylic oxalate."

Specimen No. 2.—This sample was kindly furnished, in a raw state, by Mr. JOHN WILLIAMS, President of the Pharmaceutical Society. It had been prepared from oil of winter-green. After redistillation with caustic potash, and dehydration with caustic lime, it was rectified, and found to boil between 66° and 66°·5. As it possessed a faint, sweet smell, it was manifestly impure, the impurity doubtless being a small quantity of some essential oil not capable of saponification. The somewhat longer spectrum of this substance favoured the belief that a specimen of absolute purity would be nearly photographically transparent. The specimen examined by M. SORET transmitted very little beyond the line 18 Cd, and was therefore not of such purity as this, since only 10 m.m. or about half the thickness of liquid was examined.

Specimen No. 3.—About a kilogramme of oxalate of methyl, beautifully crystallised and perfectly white, was decomposed by strong soda solution, which was made from pure soda prepared from sodium. Repeated rectifications from lumps of soda yielded more than 200 grammes of methylic alcohol, which, as it gives a spectrum showing almost as great a transparency as water, must be regarded as absolutely pure. It boils at 66° C., and has neither colour, odour, nor distinctive taste. Two photographs of this specimen are represented in the diagram; the longer spectrum resulted from the use of indium and zinc points. It shows how very nearly the alcohol approaches water in transparency.

Ethylic Alcohol. Specimen No. 1.—This specimen was obtained from Mr. KAHLBAUM, of Berlin. After rectification it boiled at 78°·5. It exhibits slightly less transparency than methylic alcohol.

Specimen No. 2.—A sample of ordinary commercial absolute alcohol obtained from Messrs. BURGOYNE and BURBIDGES, BP. 79°. We tested two or three Winchester quarts of this liquid and made use of it for dissolving such substances as were insoluble in water. They yielded the same spectrum as Nos. 1 and 2. Several other samples we have examined are not of such great purity, although from the same firm.

Propylic Alcohol.—This was carefully purified and redistilled, BP. 97°·5. It is a substance very difficult to dehydrate completely, but, as a trace of water does not affect its diactinic quality, this may be disregarded. It will be seen by a glance at the diagram that one cell-full of the liquid is less diactinic than ethylic alcohol, and that the absorption due to three times the thickness of one cell is not much greater than that caused by one cell only. As the specific volumes of the three alcohols are as the following numbers :—

Methyl	40·8
Ethyl	62·8
Propyl	84·8

we may examine the liquids in what are nearly molecular proportions by taking layers of liquid differing in thickness in the proportions of 2, 3, and 4 according to the number of carbon atoms in the molecule. It will be seen that these three substances show a gradual increase in the absorption of the more refrangible rays corresponding to the size of their molecules, or, in other words, to the number of carbon atoms they contain. The increased absorption is perfectly evident whether we take equal volumes of the liquids or thicknesses proportional to their specific volumes, from which we may conclude that one cell-full of liquid exerts nearly the maximum amount of absorption of the substance.

Normal Octylic Alcohol.—It has been shown that this substance is obtainable from the oil of *Heracleum Spondylium.* This specimen was prepared from heracleum oil by Mr. KAHLBAUM. After purification it boiled at 192°·5 instead of at 198°, the correct boiling point. One cell-full of the liquid exerts a marked degree of absorption, though, judging from the alcohols previously examined, the spectrum is very much what one might expect from a substance containing as many as eight carbon atoms.

It is worth remarking that the impure specimens of methylic and ethylic alcohols, when diluted with an equal or double volume of water, were perfectly diactinic.

The Fatty Acids.

Formic Acid. Specimen No. 1.—This acid was evidently very carefully prepared and of great purity ; it was said to be crystallisable at 48° F., though we did not succeed in obtaining it in the solid form. Obtained from Mr. KAHLBAUM.

Specimen No. 2.—Another sample similar to No. 1, obtained from Messrs. HOPKIN and WILLIAMS.

Specimen No. 3.—Prepared by us from a beautifully crystallised specimen of formiate of lead, by decomposing the salt, after drying it at 130° C., in a current of pure dry sulphuretted hydrogen, and subsequent distillation from a further quantity of formiate of lead crystals.

Specimen No. 4.—Consisted of two or three portions of the acid fractionally distilled during the preparation of the substance from oxalic acid and glycerin.

All these specimens were manifestly impure, for they yielded spectra in which the more refrangible rays were absorbed to a varying extent in every case, the absorption being considerable. The acid prepared from the lead salt by means of sulphuretted hydrogen gives the shortest spectrum and probably contains some sulphur compound. We have been much troubled by repeated attempts to prepare pure formic acid. It was decided, if possible, to oxidise pure methylic alcohol to the acid. When bichromate of potash and sulphuric acid are used for the purpose there is a danger of oxidising the acid to carbonic acid ; and when we consider, too, that in order to oxidise 16 grammes of alcohol a litre of a solution of the bichromate salt is required, it is easily seen that the formic acid will be diluted so largely that in the process of separation by distillation the product would be destroyed—at any rate this method was unsuccessful. The action of sulphuric acid and manganic oxide or tartaric acid does not yield a pure substance. The action of oxalic acid on formiate of barium yields a distillate which at first is different from the product of other processes in being free from a slight but peculiar odour, and which it is highly probable is not proper to formic acid, but belongs to some ever present impurity. On continuing the distillation, the usual smell was developed, which fact seems to show that heat causes a change in the formic acid. It is said by LORIN (*vide* WATTS' 'Dictionary of Chemistry,' vol. vi.) that formic acid of 87 per cent. can be obtained by the dry distillation of cupric formate. It is quite true that a small quantity of very weak formic acid can be obtained by this process, but as soon as all the crystalline water has been distilled off no yield of formic acid is obtainable from the salt. The products of the action of heat on the dried salt when maintained at a temperature of 200° in a paraffin bath, are metallic copper, carbonic acid and water, and, in all probability, carbon monoxide is formed.

The specimens of formic acid examined by Dr. MILLER and by M. SORET give much shorter spectra than ours. The formic acid examined by the latter observer absorbed all the rays beyond the 8th cadmium line, while the two better of our specimens transmit rays to a distance midway between the 12th and 17th lines (see Diagram 2), and that too through double the thickness of liquid.

Acetic Acid.—Two or three specimens of the glacial acetic acid of commerce were examined, as well as specimens carefully purified by distillation and crystallisation. The spectra were the same in each case, transmitting rays just beyond 17,

Propionic Acid. Specimen No. 1.—This was a very good sample of the acid, boiling at 140°–141° after rectification.

Specimen No. 2.—This was prepared from the nitrile. Boiling point 141°.

Specimen No. 3.—This was a fraction of the distillate from No. 2. It boiled at 139°–141°. These three specimens do not greatly differ in the length of transmitted spectrum; the two acids prepared from the nitrile are more diactinic than the other. The acid examined by M. SORET corresponds well with these.

Butyric Acid.—No. 1 boils at 161°·5–162°, No. 2 at 160°–161°·5. Both portions are very nearly the same in diactinic property, and equal thicknesses of the liquid being taken they do not differ much from the propionic acids.

The specific volumes of these four fatty acids are the following:—

Formic acid	42
Acetic	64
Propionic	86
Butyric	108

Consequently we must examine thicknesses of liquid proportional to these numbers in order to see the change in diactinic property corresponding to molecular differences. Since, however, we have not been able to obtain pure formic acid we have very carefully crystallised formate of sodium and compared it with sodium salts of those acids, molecular weights of the salts being dissolved and made up to equal volumes of liquid. One of the purest specimens of the sodium formate was prepared from a beautifully crystallised copper salt which had been completely dried and heated to near the temperature at which it decomposes. This was dissolved in water and mixed with a solution of carbonate of soda in just sufficient quantity to precipitate the copper. A little cupric hydrate remained dissolved, and was separated by electrolysis in a platinum dish with the aid of one of GROVE's cells. The aqueous solution of the sodium salt was slightly yellowish, but a beautifully white product was obtained by precipitation from a highly concentrated liquid by the addition of pure absolute alcohol, in which the formate is much less soluble than in water. The crystalline precipitate was recrystallised from alcohol. Notwithstanding, however, the excessive care with which sodium formate was prepared, it was found practically impossible to obtain it in a state of sufficient purity to make it available for trustworthy observation. Crystals of snow-like whiteness yielded yellowish solutions soon becoming yellow; various crops of such crystals gave spectra of different lengths; sometimes the portion giving the longest spectrum, after the most careful recrystallisations would transmit only half the rays, and by no artifice could a fraction be made to transmit the original spectrum of the salt. A very careful examination showed us that formate of soda is changed with extreme ease into oxalate, and there is no doubt that from this fact arises the unsuccessful issue of our experiments on this salt. The solution of the four sodium salts contained the following weights of the substances:—Formate,

4·8 grammes; acetate, 6·1; propionate, 7·4, and butyrate, 8·7 grammes in each 12 c.c. of liquid, or the solutions of acetate, propionate, and butyrate contained 50·8, 61·6, and 72·5 per cent. of the respective salts. The acetate and propionate formed supersaturated solutions.

Single and double thicknesses of liquid were examined. In Diagram No. 2 is shown the effect on the ultra-violet rays of the spectrum due to three successive members of a homologous series of acids. Each solution contained a molecule of the sodium salt of the acid. The two series of observations 1 and 2 represent the action of single and double cells or thicknesses of $\frac{3}{4}$ and $1\frac{1}{2}$ inch respectively. It is particularly striking how the second series of observations shows a regular decrease in transmitted rays caused by each increment of CH_2 in the molecule.

The same fact is again noticeable in Diagram No. 3, Plate 23. Here, in order to get rid of the inconvenience caused by the change of alkaline formates into oxalates on evaporation, we made use of very beautiful specimens of barium salts. In this case the formate is the most transparent of salts, and it may be seen that the acetate bears the same relation to it in transparency that in the case of the sodium salt the propionate bore to the acetate.

A glance at Diagram No. 3 will show that a cell-full of the acids corresponding to the ethylic and propylic alcohols, which we have every reason to believe are perfectly pure substances, are less diactinic than the alcohols as shown in Diagram No. 1, which fact points to the carboxyl group in the molecule possessing a special absorptive power greater than that of hydroxyl. We have further evidence of this in the short spectrum of oxalic as compared with acetic acid. The specimen examined was prepared with great care and repeatedly recrystallised. There is every reason to believe in its absolute purity.

The Ethereal Salts of Fatty Acids.

In examining regular series of formates, acetates, propionates, &c., of the radicles, methyl, ethyl, and propyl, it was expected that probably the majority of substances would be of such a degree of purity that some relation between their constitution and their optical properties would be traceable. About twenty specimens of these compound ethers were obtained from Mr. KAHLBAUM; they varied in quantity according to the nature of the substances, but the majority of the specimens weighed 50 grammes. They were purified by washing with distilled water and with carbonate of potash; they were dried by standing over fused carbonate of potash, and were subsequently distilled. The boiling points of the various specimens examined are given on Diagram No. 4.

It will be seen that it was hopeless to get any result from this examination, many of the substances manifestly containing impurities which injured their photographic transparency. The only three bodies which appear to be pure are the ethylic acetate,

propionate, and butyrate. Even in this case two specimens of the same substance, with precisely the same boiling point, vary slightly in diactinic quality. Unless very large quantities of liquid are operated upon, substances cannot be purified by fractional distillation, and even under most favourable circumstances distillation must be several times repeated. The remarkably short spectrum transmitted by amyl-butyrate was due evidently to some impurity, since the behaviour of the substance on dilution with alcohol was quite in accordance with this view. The generally transparent character of the alcohols and ethereal salts is remarkable.

Normal Hydrocarbons.

Only three of these—hexane, heptane, and octane—have been examined; they were specimens kindly lent us by Prof. SCHORLEMMER, and believed to be perfectly pure. Three series of photographs were taken of them, but they yielded spectra in no way corresponding to their difference in composition, from which we are inclined to believe they were impure (see Diagram No. 2).

Compound Ammonias.

A series of five of these bodies was examined, the solutions containing 33 per cent. of the substances in the case of ethylamine and methylamine. It is believed that, with the exception of ethylamine, they contained some impurity, since the methylamine and dimethylamine yielded shorter spectra than the ethylamine. These were commercial samples, and most probably were prepared from ammonia obtained from gas-liquor. M. SORET has shown that commercial ammonia, even after many recrystallisations as sulphate, still shows an absorption band, due to some impurity which is constantly present; it is therefore scarcely likely that pure products would be obtained unless specially prepared ammonia be used for the purpose. We considered that the volcanic ammonia, which is free from some of the impurities present in that made from gas-liquor, might be perfectly diactinic. Three separate samples, each measuring half a gallon, were examined, with the result that all the rays beyond 17 Cd were cut off. Even when so dilute that only one volume of ammonia was contained in 64 of water, all traces of absorption had not been destroyed (see Diagram No. 5, Plate 25). This absorption is not due to nitric acid, because M. SORET has shown that the absorption band due to that substance occurs between 12 Cd and 17 Cd.

Conclusions.

(1.) The normal alcohols of the series $C_nH_{2n-1}OH$, are remarkable for transparency to the ultra-violet rays of the spectrum, pure methylic alcohol being nearly as much so as water.

(2.) The normal fatty acids exhibit a greater absorption of the more refrangible rays of the ultra-violet spectrum than the normal alcohols containing the same number of carbon atoms.

(3.) There is an increased absorption of the more refrangible rays corresponding to each increment of CH_2 in the molecule of the alcohols and acids.

(4.) Like the alcohols and acids the ethereal salts derived from them are highly transparent to the ultra-violet rays, and do not exhibit absorption bands.

PART II.

Examination of Substances containing the Benzene Nucleus.

In the examination of such substances as contain a closed chain of carbon atoms doubly linked together, one fact presented itself in a striking manner. All these bodies are strongly adiactinic, those which are the least so being the hydrocarbons; Diagram No. 2, will at once make this apparent. Professor STOKES has pointed out that one of these substances, salicine, in an aqueous solution, the strength of which is not stated, shows a characteristic absorption band. Now salicine is a substance the constitution of which is perfectly well known: it is a glucoside of saligenin,

$$\left.\begin{array}{l} C_6H_{11}O_5 \\ C_6H_4(OH)CH_2 \end{array}\right\} O$$

and consequently the absorption band may be due to the saligenin. At any rate it seemed worth while to dilute solutions of known strength, containing such allied substances as phenol, salicylic acid and salicylate of methyl, and ascertain whether any absorption bands are thus made visible. The result has disclosed the fact that almost if not entirely all benzene derivatives, including the hydrocarbon itself, are characterised by one or more absorption bands, which resist modification or extinction by dilution to an enormous extent.

For this part of the research it has been necessary to make solutions of known strength, to dilute them with definite quantities of water, and photograph the various liquids thus obtained. These photographs have been placed upon sectional paper, upon which the lines of cadmium as seen in a photograph of the metallic spectrum have been drawn, and the proportions of substance in solution have been co-ordinated with the position of the absorption bands relative to the cadmium lines. A series of curves has thus been obtained, and each of these proves to be a highly characteristic feature of the substance observed. The number of photographs necessary for completing the curves has varied very much with different substances, sometimes four or five, and occasionally eighteen or twenty have been taken.

When the substance to be examined was a liquid, two cubic centimetres were measured and diluted with alcohol if necessary, or water if possible, so as to form a total volume of 100 c.c. From this solution others more dilute were obtained. If the

substance were a solid 0·2 gr. or 0·02 gr. in weight of the body were dissolved in alcohol or water so as to form a total volume of 100 c.c., and when it was desirable to compare a liquid substance with a solid, both were weighed and dissolved in the same manner. In this way salicylate of methyl was compared with salicylic acid and salicine.

Benzene (Diagram No. 6).—A very pure specimen, kindly lent us by Professor GUTHRIE. About ten ounces of the substance had been separated from more than a gallon and a-half of the commercial benzene, by successive crystallisations in a freezing mixture. The first feature noticeable here is the small alteration in the absorption of the rays caused by a dilution with 99 volumes of alcohol. It is impossible to describe the changes noticed on repeated dilutions without reference to the diagram, but it may be well to record the proportions of alcohol to benzene in the liquids photographed.

One part of benzene was successively diluted so as to measure 100, 150, 190, 220, 235, 250, 375, 500, 750, 850, 1000, 1275, 1500, 2000, and 2500 times its original volume. With a dilution of 750, six absorption bands are seen. In other words, as the cell is $\frac{3}{4}$ inch in thickness, a layer of benzene $\frac{1}{1000}$th of an inch in thickness would show the same spectrum. As the bands are perfectly well seen after a dilution of 1500 times, it follows that a film of benzene $\frac{1}{2000}$th of an inch in thickness would show them.

Toluene.—Methylbenzene, BP. 111° C.—The various solutions examined contained $\frac{1}{100}$, $\frac{1}{500}$, $\frac{1}{1000}$, $\frac{1}{2000}$, $\frac{1}{2500}$, and $\frac{1}{3000}$ of their volume of the hydrocarbon. It is evident, from Diagram No. 7, that a similarity exists between this substance and benzene, though fewer rays are transmitted by toluene, which greatly modifies the appearance of the two diagrams. The two absorption bands between 17 Cd and 18 Cd are highly characteristic.

Ethylbenzene, BP. 135°–6 (Diagram 8).—The solutions examined contained the following volumes of the liquid, $\frac{1}{150}$, $\frac{1}{300}$, $\frac{1}{500}$, $\frac{1}{1000}$, $\frac{1}{2000}$, $\frac{1}{3000}$, $\frac{1}{3500}$, $\frac{1}{4000}$, and $\frac{1}{6000}$. At $\frac{1}{500}$ a strong band of transmitted rays appears from about half way between 18 Cd and 23 Cd, and extends to 24 Cd; this widens out, until at $\frac{1}{3000}$ it meets the narrow absorption band noticed in the previous spectrum as situated between 17 Cd and 18 Cd.

Trimethylbenzene.—Mesitylene.—The methyl molecules occupy the position indicated by 1–3–5, BP. 163–4° C. (Diagram No. 9). Observations were made on solutions containing $\frac{1}{240}$, $\frac{1}{500}$, $\frac{1}{1000}$, $\frac{1}{2000}$, $\frac{1}{3000}$, $\frac{1}{6000}$ and $\frac{1}{10000}$ of their volume of the liquid. A transmitted band occurs between 18 Cd and 23 Cd, commencing at $\frac{1}{500}$ dilution. At $\frac{1}{2000}$ two narrow bands of transmitted rays occur between 17 Cd and 18 Cd.

These hydrocarbons are the least opaque to the photographic rays of the many substances containing the benzene nucleus which we have examined, although compared with the substances previously treated of, namely, the alcohols, fatty acids, and ethereal salts, they are greatly wanting in transparency.

We now pass to substances containing the hydroxyl group replacing hydrogen.

Phenol, $C_6H_5.OH$ (Diagram No. 10).—Solutions in water containing the following quantities of the body were examined: $\frac{1}{400}$, $\frac{1}{800}$, $\frac{1}{1700}$, $\frac{1}{3200}$, $\frac{1}{6400}$, $\frac{1}{12800}$, and $\frac{1}{25600}$.

In this case, as in all the following, the intensity of all the absorption bands renders it necessary to reduce the dimensions of the ordinates to the curve, which represent the quantities of water used in dilution, otherwise the diagram would stretch to five times the length of those representing the hydrocarbons. The absorption of the rays more refrangible that 24 Cd was not extinguished by the dilution to $\frac{1}{12800}$, nor is it entirely destroyed by doubling such dilution.

Thymol (Diagram No. 11).—This body is a methyl-iso-propyl-oxybenzene,

$$C_6H_3\begin{cases} OH \\ CH_3 \\ CH(CH_3)_2 \end{cases}$$

Solutions of the following strength were examined: 1 gramme was contained in 100 c.c., 1000 c.c., 2000 c.c., 5000 c.c., 7500 c.c., 10,000 c.c., 20,000 c.c., 40,000 c.c., 80,000 c.c., 100,000 c.c.

The smaller effect of dilution on the absorption rendered it necessary again to reduce the dimensions of the ordinates to half those of the phenol curves.

It seems as if complexity of structure increases the intensity of the absorption bands.

Pyrogallol, C_6H_3 $(OH)_3$ (Diagram No. 12).—Solutions containing the following proportions of the substance were examined: $\frac{1}{500}$, $\frac{1}{1000}$, $\frac{1}{5000}$, $\frac{1}{10000}$, $\frac{1}{50000}$; $\frac{1}{75000}$, and $\frac{1}{100000}$. After dilution has reduced the proportion of substance in solution to $\frac{1}{5000}$, rays beyond 18 Cd are faintly transmitted, with a proportion of $\frac{1}{50000}$ there is nearly complete transmission as far as 23 Cd, but there is still some absorption with $\frac{1}{100000}$.

Benzoic, hippuric, and phthalic acids being substances in which the carboxyl group occurs, are of much interest.

Benzoic Acid, $C_6H_5.COOH$ (Diagram No. 13).—Solutions containing $\frac{1}{200}$, $\frac{1}{1000}$, $\frac{1}{3000}$, $\frac{1}{5000}$, $\frac{1}{6000}$, $\frac{1}{8000}$, $\frac{1}{10000}$, $\frac{1}{15000}$, $\frac{1}{20000}$, $\frac{1}{40000}$, $\frac{1}{80000}$, and $\frac{1}{120000}$ their weight of substance were examined.

The most diluted of these liquids still partially absorbed the rays beyond 23 Cd—that is to say, they were enfeebled. There is a feeble transmission of the rays between 17 Cd and 18 Cd with a dilution of $\frac{1}{5000}$. This extends to the main band of transmitted rays at $\frac{1}{6000}$, and a continuous spectrum is transmitted as far as 18 Cd with $\frac{1}{15000}$.

Phthalic Acid, $C_6H_4.(COOH)_2$ (Diagram No. 14).—The general appearance of this and the preceding spectrum is remarkable, though there is a distinct difference between them. Solutions containing $\frac{1}{100}$, $\frac{1}{1000}$, $\frac{1}{5000}$, $\frac{1}{6000}$, $\frac{1}{7500}$, $\frac{1}{10000}$, $\frac{1}{15000}$, $\frac{1}{20000}$, $\frac{1}{40000}$, $\frac{1}{60000}$, $\frac{1}{80000}$, $\frac{1}{100000}$, $\frac{1}{120000}$, $\frac{1}{150000}$, $\frac{1}{200000}$, $\frac{1}{250000}$, $\frac{1}{300000}$, and $\frac{1}{400000}$ths. their weight were examined. The last solution on comparison with distilled water still showed a slight absorption of the extreme rays. It is the increased opacity of the latter substance which constituted the chief difference between the spectra of

benzoic and phthalic acids. This strengthens the view already expressed, that the introduction of the carboxyl group into a molecule increases the actinic absorption, phthalic acid standing to benzoic as oxalic to acetic acid, while benzoic acid and phenol are related in the same manner as acetic acid and alcohol.

Hippuric Acid, $C_9H_9NO_3$, (Diagram No. 15).—This being a benzamido-acetic acid it was interesting to ascertain whether the benzoic acid residue was traceable; its peculiarities, however, do not appear. Solutions examined contained $\frac{1}{500}$, $\frac{1}{2000}$, $\frac{1}{5000}$, $\frac{1}{10000}$, and $\frac{1}{40000}$ of their weight of the substance.

Aniline, $C_6H_5.NH_2$, BP. 182° (Diagram No. 16).—Solutions of aniline in alcohol were made which were afterwards diluted with water. Solutions containing the following proportions by volume of aniline were examined: $\frac{1}{1000}$, $\frac{1}{10000}$, $\frac{1}{12000}$, $\frac{1}{15000}$, $\frac{1}{20000}$, $\frac{1}{30000}$, $\frac{1}{100000}$, $\frac{1}{110000}$, $\frac{1}{120000}$, $\frac{1}{180000}$, and $\frac{1}{220000}$. A first absorption band lies immediately below 17 Cd; it first makes a definite appearance when the rays just beyond have been transmitted after a dilution with 12,000 parts of water. The absorption is not destroyed by carrying the dilution $\frac{1}{30000}$. No rays are transmitted further than midway between 18 Cd and 23 Cd until a dilution of $\frac{1}{110000}$ is attained, and all absorption of the more refrangible rays is not effected until after dilution with 220,000 parts of water.

One of the chief objects in view in commencing a study of the benzene derivatives was to ascertain the difference in the absorption spectra of strictly isomeric substances. We have accordingly examined the three oxybenzoic acids, two nitro-phenols, and two nitranilines.

Salicylic Acid, $C_6H_4.OH.COOH$, *or* 1·2 *Oxybenzoic Acid* (Diagram No. 17).—This substance, prepared some years ago by one of us from the oil of winter-green, was in the form of large crystals. We recrystallised it from alcohol, and took the choicest crystals for preparing our solutions. Solutions were made containing $\frac{1}{200}$, $\frac{1}{300}$, $\frac{1}{400}$, $\frac{1}{800}$, $\frac{1}{1000}$, $\frac{1}{1700}$, $\frac{1}{2000}$, $\frac{1}{3000}$, $\frac{1}{3200}$, $\frac{1}{4000}$, $\frac{1}{4400}$, $\frac{1}{4500}$, $\frac{1}{4700}$, $\frac{1}{5000}$, $\frac{1}{6000}$, $\frac{1}{8000}$, $\frac{1}{10000}$, $\frac{1}{15000}$, and $\frac{1}{20000}$ of their weight of the substance. There is nothing remarkable in the spectrum until after a dilution of $\frac{1}{1000}$; from this point, however, until $\frac{1}{5000}$ is reached, the curves obtained are very curious.

Oxybenzoic Acid, 1·3 (Diagram No. 18).—This compound is remarkable for its adiactinic quality; it transmits no rays beyond 12 Cd until after a dilution of $\frac{1}{5000}$, and there is still a distinct absorption between 12 Cd and 17 Cd until $\frac{1}{20000}$, when even the rays beyond 18 Cd are only feebly transmitted.

Paroxybenzoic Acid, 1·4 (Diagram No. 19).—This acid shows an increase in adiactinic quality exceeding that of the preceding substances. Solutions containing $\frac{1}{13000}$, $\frac{1}{26000}$, $\frac{1}{39000}$, $\frac{1}{52000}$, $\frac{1}{77000}$, $\frac{1}{103000}$, $\frac{1}{154000}$, $\frac{1}{205000}$, and $\frac{1}{140000}$ their weight of the substance were examined, and the diagrams constructed from these two other sets of observations were, however, taken with various proportions of solid to solution; they gave, however, the same result. No rays beyond 17 Cd are transmitted until after a dilution of $\frac{1}{30000}$ has been reached. There is a broad absorption band between

18 Cd and 23 Cd, with one part of the substance in 100,000 of water, and this band continues, though diminished in power, until 205,000 parts of water have been added. Absorption of the more refrangible rays beyond 26 Cd continue till 410,000 parts of water have been used in dilution. Had this diagram been drawn on the same scale as that representing benzene and the allied hydrocarbons, it would have extended beyond a length of 170 feet, each inch only of which would have represented a dilution with 200 parts of water.

The two following substances were examined on account of their close relationship to salicylic acid and its isomers :—

Salicylate of Methyl, $C_6H_4.OH.COOCH_3$, BP. 220°·7 (Diagram No. 20).—This was rectified from about a kilogramme of oil of winter-green. Two sets of observations were made, and solutions containing the following proportions by weight of the substances were used : $\frac{1}{1000}$, $\frac{1}{1500}$, $\frac{1}{2500}$, $\frac{1}{5000}$, $\frac{1}{10000}$, $\frac{1}{15000}$, $\frac{1}{30000}$, $\frac{1}{45000}$, and $\frac{1}{60000}$. At first, all rays beyond 12 Cd are absorbed, and this condition continues until beyond a dilution of $\frac{1}{1500}$, when the rays between 17 Cd and 18 Cd are transmitted. The absorption band lying between 12 Cd and 17 Cd becomes nearly extinguished by an addition of 45,000 parts of the diluent; but at the same time a second band of rays, lying between 25 Cd and 26 Cd, is transmitted, which gradually extends but does not overcome the absorption band lying between 18 Cd and 23 Cd until after a dilution with 60,000 parts of water.

Salicine, $\left.\begin{matrix} C_6H_{11}O_5 \\ C_6H_4(OH)CH_2 \end{matrix}\right\} O$ (Diagram No. 21).—Solutions examined contained the following proportions of substance: $\frac{1}{400}$, $\frac{1}{800}$, $\frac{1}{1600}$, $\frac{1}{4000}$, $\frac{1}{8000}$, $\frac{1}{20000}$, and $\frac{1}{50000}$. The absorption band is highly characteristic. Transmitted rays, a little less refrangible than 23 Cd, make their appearance in solutions containing $\frac{1}{400}$ of substance, in addition to the continuous transmission of rays less refrangible than 17 Cd. In solutions containing $\frac{1}{8000}$ the absorption band has practically disappeared.

Ortho-nitro-phenol, $C_6H_4.NO_2.OH$, 1·2 (Diagram No. 22).—Aqueous solutions only of the phenols were employed notwithstanding their very slight solubility in water. Solutions containing $\frac{1}{4000}$, $\frac{1}{8000}$, $\frac{1}{12000}$, $\frac{1}{16000}$, $\frac{1}{20000}$, $\frac{1}{25000}$, $\frac{1}{28000}$, $\frac{1}{30000}$, $\frac{1}{32000}$, $\frac{1}{35000}$, $\frac{1}{36000}$, $\frac{1}{40000}$, $\frac{1}{45000}$, $\frac{1}{50000}$, $\frac{1}{55000}$, and $\frac{1}{60000}$ of their weight of the crystals were examined.

Although this is a colourless substance it is remarkable how it cuts off nearly all but the visible rays, even when dissolved in 20,000 times its weight of water. When the dilution has reached 25,000, the rays a little beyond 11 Cd and 12 Cd are transmitted; at 35,000 a second band of rays lying between 18 Cd and 23 Cd makes its appearance; and at 60,000 there is almost a continuous spectrum nearly as far as 26 Cd, though traces of an absorption band are seen even in presence of 120,000 parts of water.

Para-nitro-phenol, 1·4 (Diagram No. 23).—This substance is strongly coloured

yellow, and more than 16,000 parts of water do not yield a solution which is colourless when an inch of liquid is examined.

Solutions were made containing the following proportions of the salt by weight:— $\frac{1}{6000}$, $\frac{1}{8000}$, $\frac{1}{16000}$, $\frac{1}{20000}$, $\frac{1}{32000}$, $\frac{1}{40000}$, $\frac{1}{50000}$, $\frac{1}{55000}$, and $\frac{1}{60000}$.

The curve representative of this substance is very remarkable. The chief features are a narrow band of transmitted rays which must be almost contained within the visible spectrum, which scarcely increases in width even in presence of 16,000 parts of water, together with a second more refrangible group of rays between 17 Cd and 23 Cd, which widens out very considerably.

Meta-nitraniline, $C_6H_4.NO_2.NH_2$, 1·3 (Diagram No. 24).—This body was observed in aqueous solution, containing the following proportions of substance: $\frac{1}{4000}$, $\frac{1}{5000}$, $\frac{1}{6000}$, $\frac{1}{7000}$, $\frac{1}{8000}$, $\frac{1}{20000}$, $\frac{1}{28000}$, $\frac{1}{40000}$, $\frac{1}{60000}$, and $\frac{1}{100000}$.

The chief feature in the curve derived from the spectra of this subtance is the long, straight, almost unaltered absorption band at about 9 Cd, which stretches from 8000 to 40,000.

There is still absorption near 23, 24, 25, and 26 Cd, in presence of 120,000 parts of water.

Para-nitraniline, 1·4 (Diagram No. 25).—Solutions containing $\frac{1}{4000}$, $\frac{1}{8000}$, $\frac{1}{16000}$, $\frac{1}{20000}$, $\frac{1}{40000}$, $\frac{1}{60000}$, and $\frac{1}{100000}$ parts by weight of the substance were examined. The general appearance of the curve representing this body resembles in a striking degree that belonging to the corresponding nitrophenol. The absorption band which in presence of 50,000 parts of water lies between the air-line and 10 Cd continues, though narrowed and much enfeebled, until double this dilution has been effected. Throughout the various dilutions the blue and violet rays were absorbed, although more refrangible rays were transmitted.

The following examples afford an instance of one of the applications of this kind of work to the purposes of research.

Tyrosine was for some time considered by BARTH and other chemists to be a derivative of paroxy-benzoic acid, but more recently it has been regarded as an oxyphenyl-amido-propionic acid,

$$C_6H_4\begin{cases} OH \\ C_2H_3(NH_2)COOH. \end{cases}$$

But these views have not been confirmed by the synthesis of the substance.

If it be a derivative of paroxy-benzoic acid it may be expected to partake of the peculiarities of this substance in its action on the ultra-violet rays of the spectrum.

We have accordingly examined solutions of tyrosine (see Diagram No. 26), and find that it more nearly resembles a phenol in actinic quality than an acid in which the carboxyl group replaces hydrogen in the benzene nucleus. Hence the latter view of its constitution, which represents the group oxyphenyl as substituting hydrogen in amido-propionic acid, is more correct than the former, since it is in accordance with its optical character.

The solutions of tyrosine examined contained $\frac{1}{500}$, $\frac{1}{1000}$, $\frac{1}{2000}$, and $\frac{1}{6000}$ of their weight of the substance.

Phlorizine (Diagram No. 27).—It was considered of interest to examine this substance, since it is a glucoside containing the residue of phloroglucin, a body isomeric with pyrogallol, and phloretic acid an oxyphenyl-propionic acid. Solutions containing the following proportions of the substance were taken : $\frac{1}{50}$, $\frac{1}{500}$, $\frac{1}{5000}$, $\frac{1}{10000}$, $\frac{1}{15000}$, $\frac{1}{30000}$, and $\frac{1}{50000}$. The absorption band is well defined and of great intensity; the second band of transmitted rays appearing at $\frac{1}{5000}$ occupies the same position as that seen in tyrosine, though there is not much resemblance between the curves of these two bodies.

It is evident that most interesting results may be anticipated from a continuation of this research, and this contribution must be accepted as rather the bare commencement of the subject than its conclusion.

The following is a summary of the chief points of interest appertaining to benzene and its derivatives :—

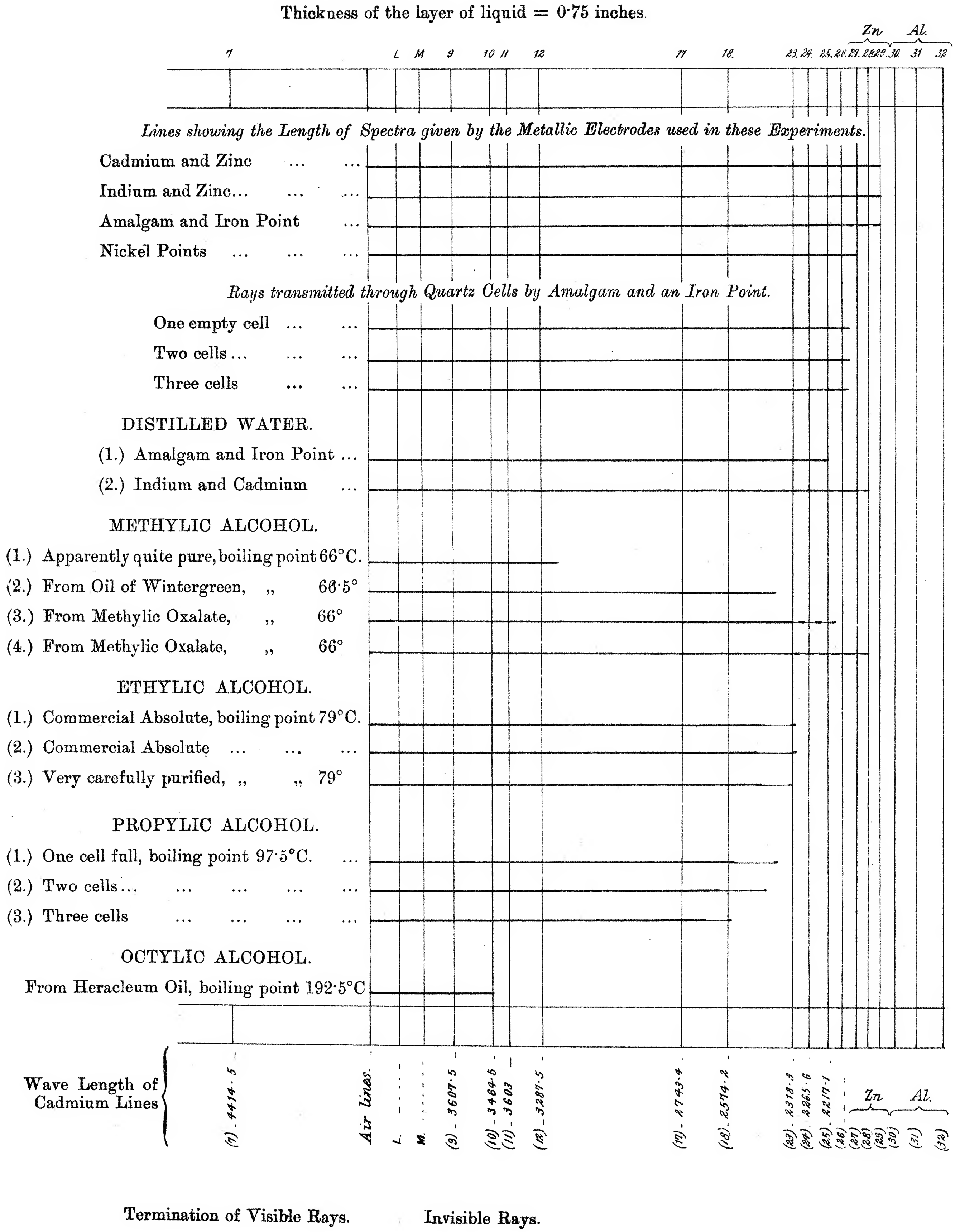
(1.) Benzene and the hydrocarbons, alcohols, acids, and amines derived therefrom are remarkable—first, for their powerful absorption of the more refrangible rays; secondly, for the absorption bands made visible by dissolving them in water or alcohol; and thirdly, for the extraordinary intensity of these absorption bands : that is to say, their power of resisting dilution.

(2.) Isomeric bodies containing the benzene nucleus exhibit widely different spectra, inasmuch as their absorption bands vary in position and in intensity.

(3.) The photographic absorption spectra can be employed as a means of identifying organic substances and as a most delicate test of their purity. The curves obtained by co-ordinating the extent of dilution, or in other words the quantity of substance, with the position of the rays of the spectrum transmitted by the solution, form a strongly marked and highly characteristic feature of very many substances.

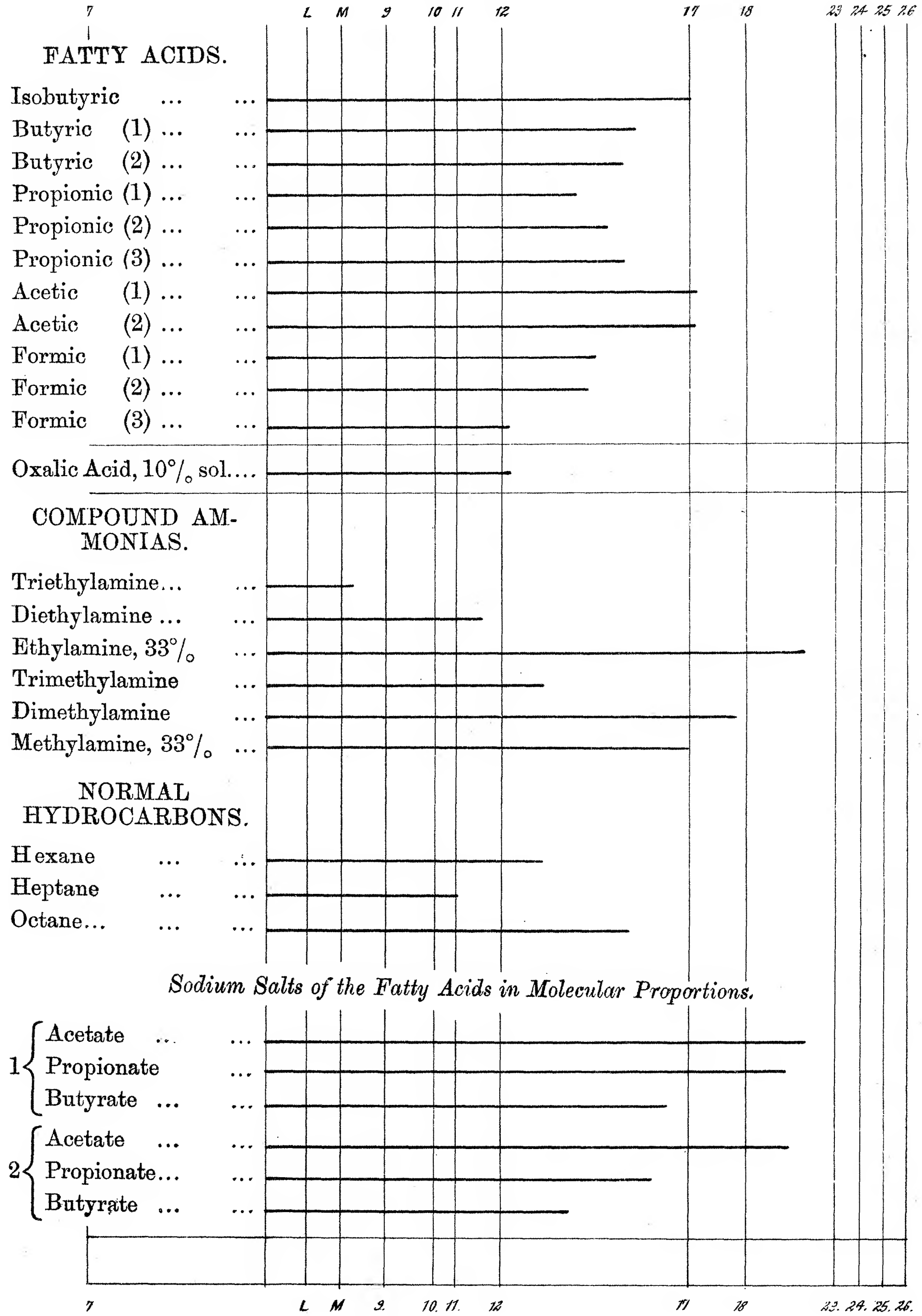
No. 1.

Diagram showing the Effect of Water and of the Alcohols on the Ultra-Violet Rays of Metallic Spectra.

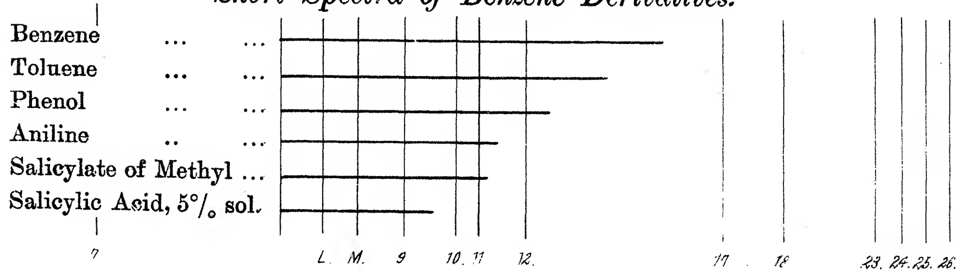


No. 2.

Diagram showing the Absorption of Ultra-Violet Rays by the Fatty Acids and other Organic Substances.

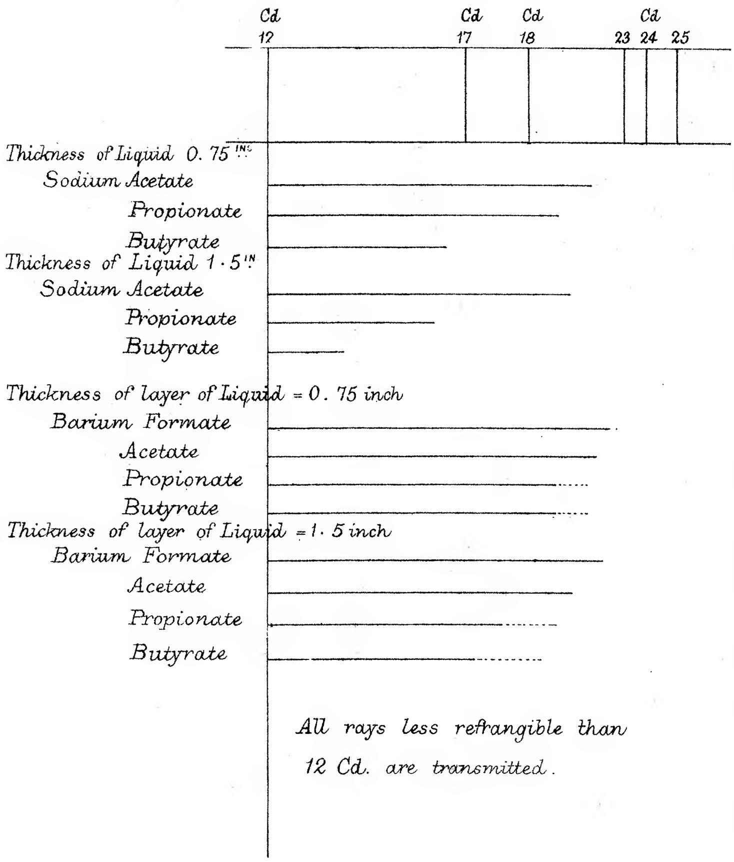


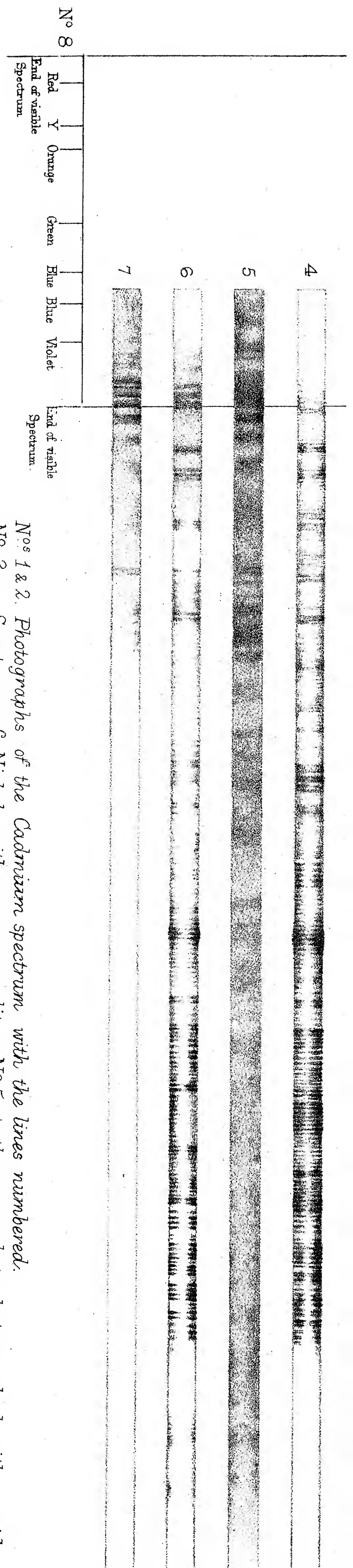
Short Spectra of Benzene Derivatives.



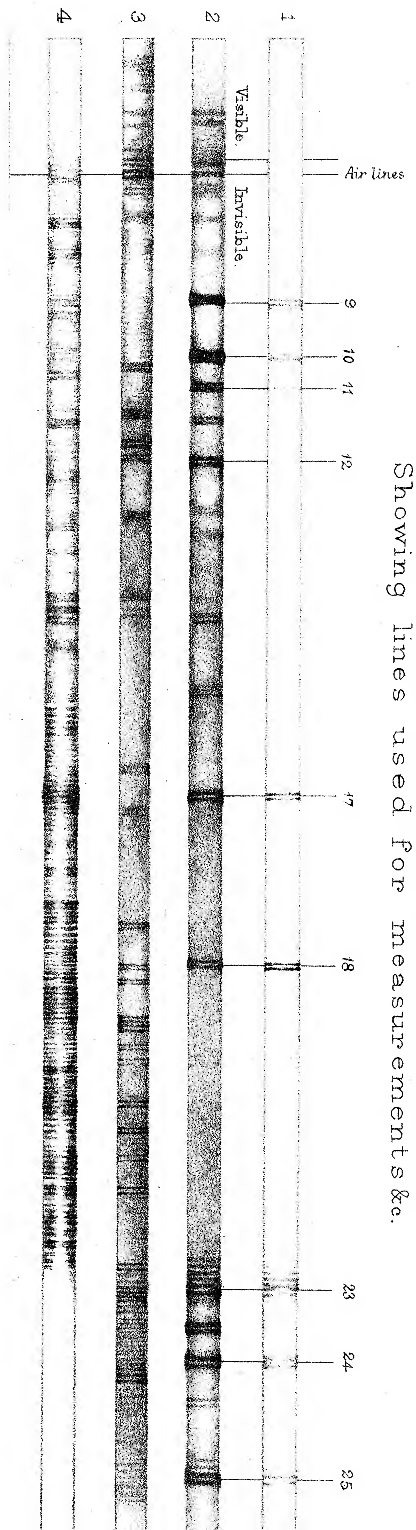
No. 3.

Diagram showing the absorption of the ultra violet rays by sodium and barium salts of the fatty Acids in molecular proportions.

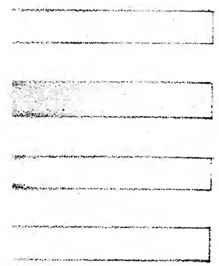




Nos 1 & 2. Photographs of the Cadmium spectrum with the lines numbered.
No 3. Spectrum of Nickel with a narrow slit. No 5. is the same, but photographed with a wide
No 4. Spectrum of Iron on a gelatine plate. No 6. the same on a Beechey plate.
No 7. Spectrum of Nickel photographed through a Nicol's prism, showing the absorption du
the film of Canada balsam
No 8. The extension of the visible rays beyond the photographic spectrum is here shown.



EXAMPLES OF ULTRA-VIOLET SPECTRA,
Showing lines used for measurements &c.



a wide slit.

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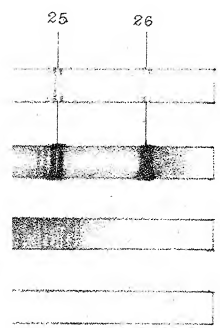
West, Newman & Co. sc.

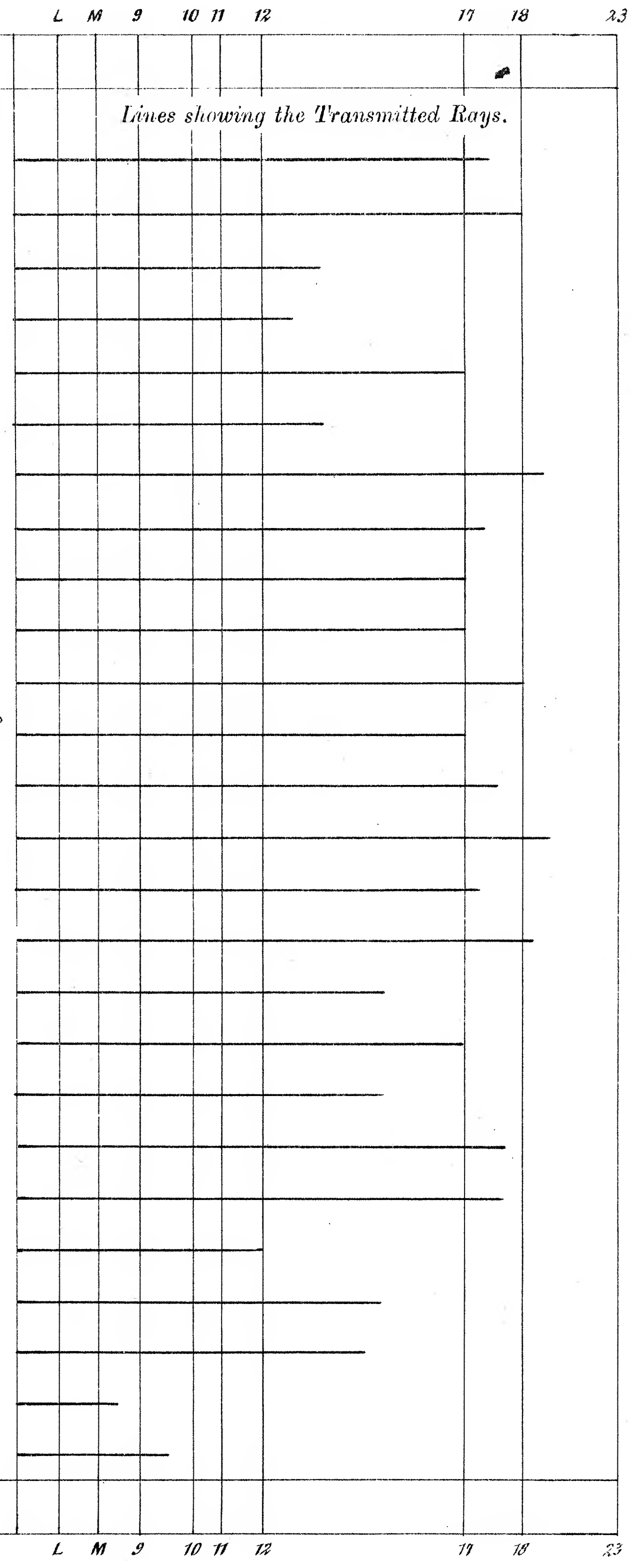

25
26

No. 4.

Diagram showing the Results of an Examination of a Series of Ethereal Salts.

Thickness of layer of liquid = 0·75 inch.

Name of Substance.	*Boiling Point.*
Methyl Formiate ...	33·5°
„ Acetate ...	57°—58°
„ Propionate ...	81°
„ Butyrate ...	
„ Valerianate ...	
Ethyl Formiate ...	54°—56°
„ Acetate ...	78·5°
„ Propionate ...	100°
„ Propionate ...	100°
„ Butyrate ...	122°—123°
„ Butyrate ...	119°
„ Valerianate ...	131°—132·5°
Propyl Formiate ...	82°
„ Propionate ...	120°—122°
„ Valerianate ...	155°—156°
Isobutyl Formiate ...	98°—98·5°
„ Acetate ...	115°
„ Butyrate ...	144°—146°
„ Butyrate ...	146°—148°
„ Valerianate...	166°—167°
Amyl Formiate ...	123°
„ Acetate ...	156°—158°
„ Propionate ...	156°—158°
„ Propionate ...	156°—158°
„ Butyrate ...	173°—174°
„ Butyrate ...	177°—179°



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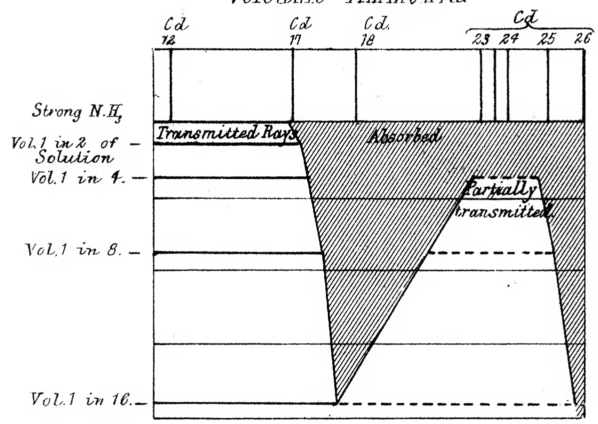
No. 5.

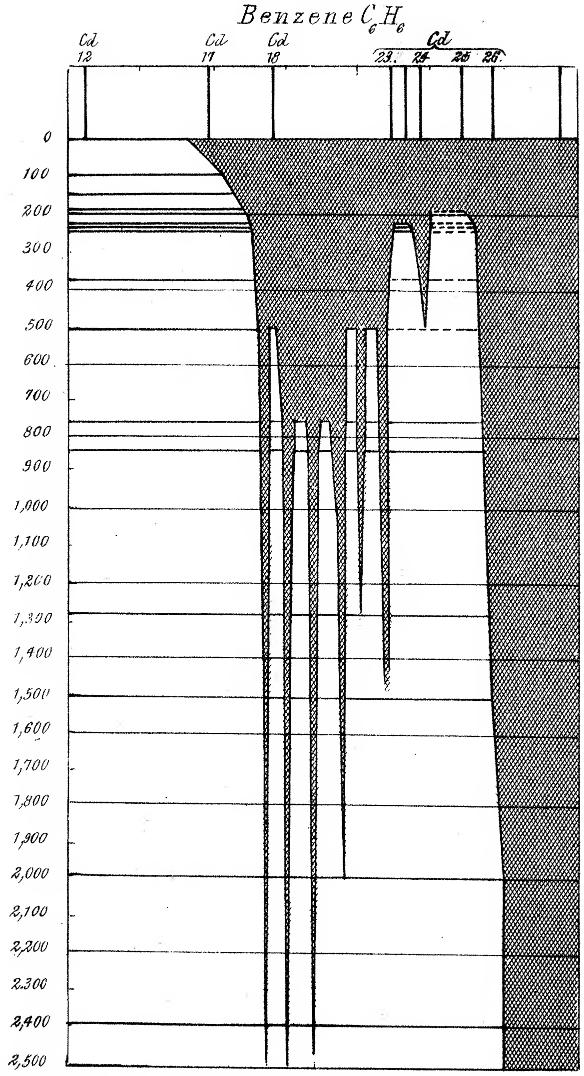
Absorption due to an impurity.
Volcanic Ammonia.



This absorption is not due to nitrous compounds since Mr Soret shows that the absorption due to nitric acid occurs between 12 and 17 Cd.

No. 6.

Benzene C_6H_6

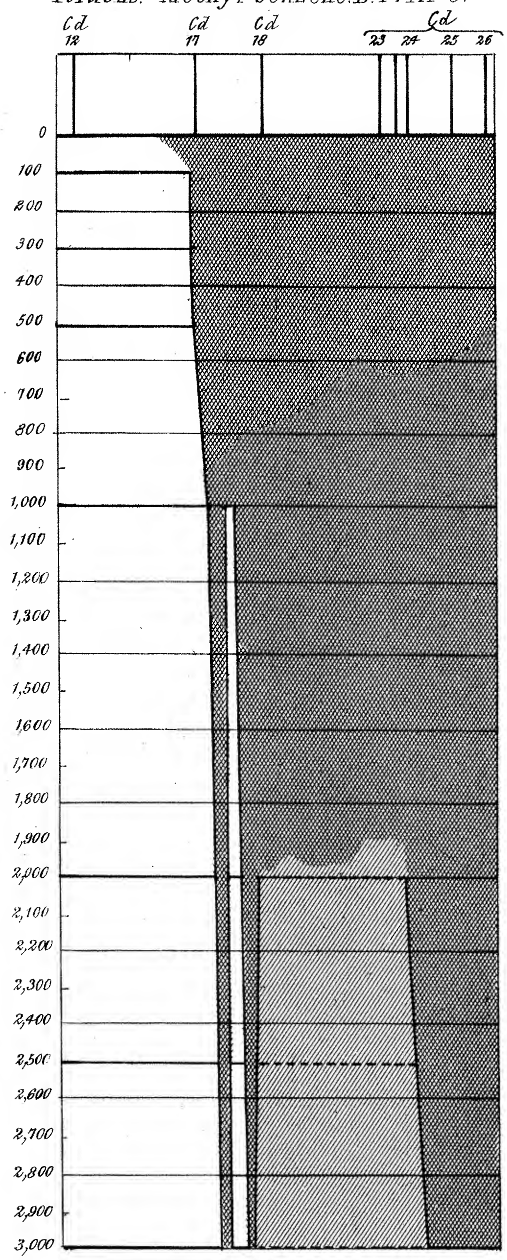


Ordinates = the proportion of liquid containing 1 volume of Benzene.

Thickness of layer of liquid = 0.75 inch.

No. 7.

Toluene. Methyl-benzene. B. P. 111° C.



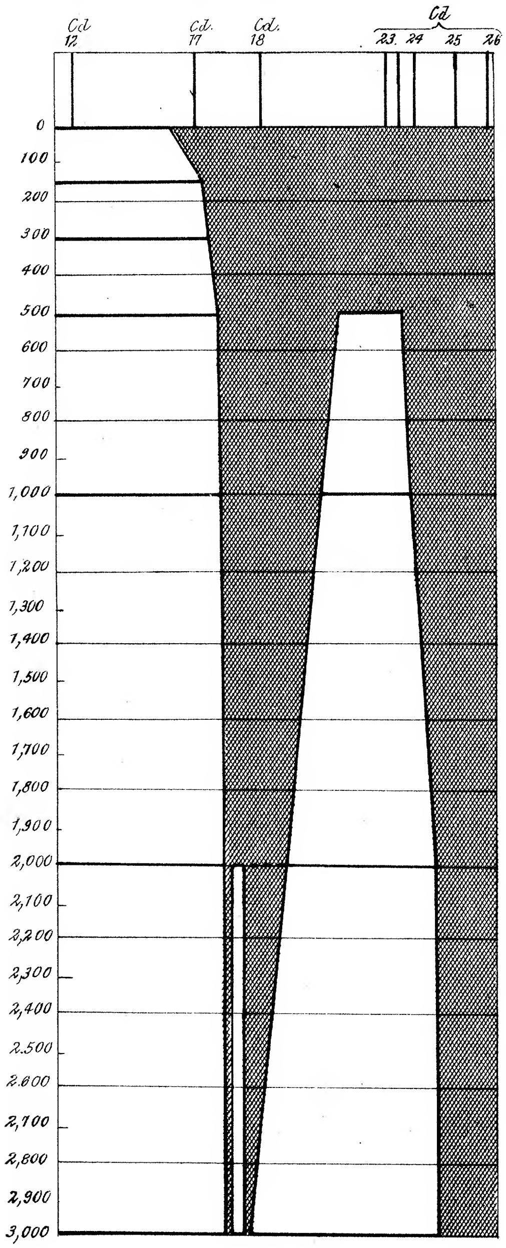
Ordinates = the porportion of alcohol containing 1 volume of Toluene.

Thickness of layer of liquid = 0·75 inch.

Harrison & Sons, Lith. St. Martins Lane, W.C.

N°8.

Ethyl-benzene $C_6H_5 . C_2H_5$ *B.P. 134°.*

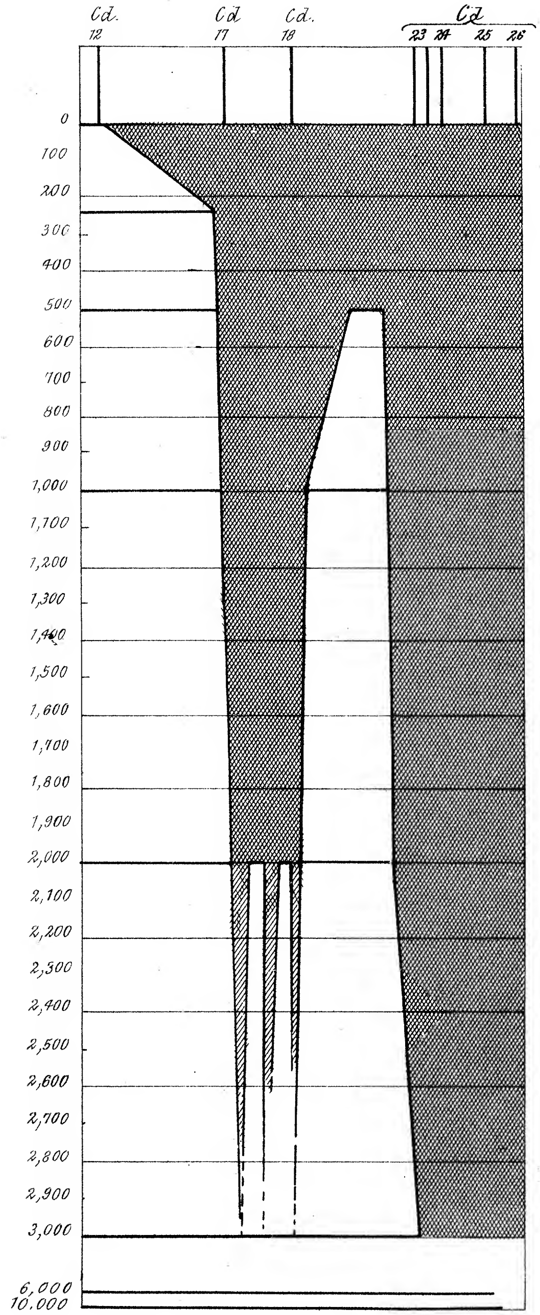


Ordinates = the proportion of alcohol to 1 part by volume of Ethyl-benzene.

Thickness of layer of liquid = 0.75 inch.

N°9.

1. 3. 5. Trimethyl-benzene $C_6H_3.(CH_3)_3$



Absorption continues till 40,000 parts of water or alcohol have been added.

Ordinates = the proportion of alcohol to 1 part by volume of Trimethyl-benzene

Thickness of layer of liquid = 0·75 inch.

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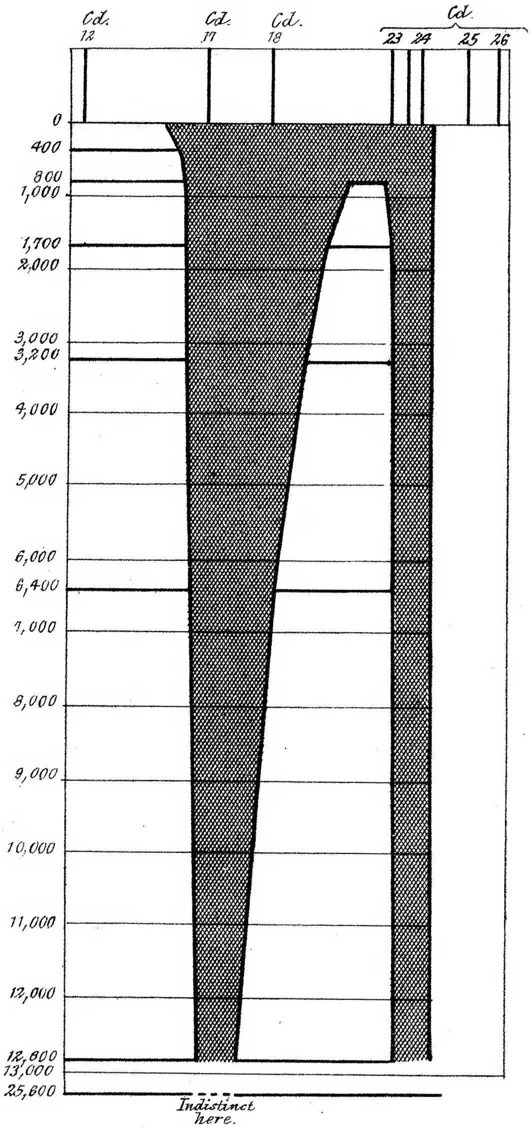
No. 10.

Phenol. $C_6H_5 \cdot OH$.

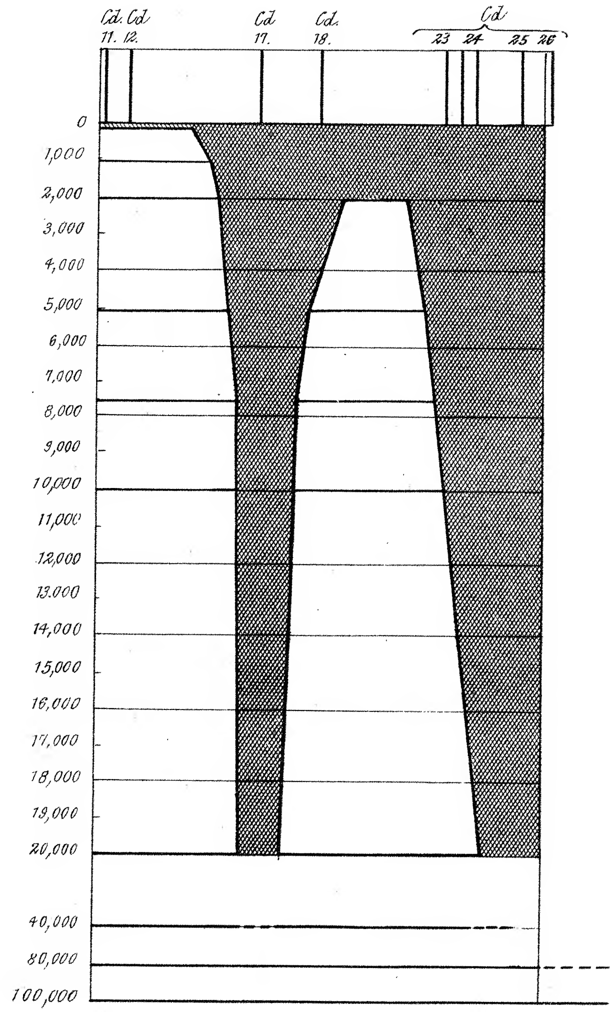


Ordinates = the proportion of water to 1 part by weight of Phenol.

Thickness of layer of liquid = 0·75 inch.

No. 11.

Thymol.

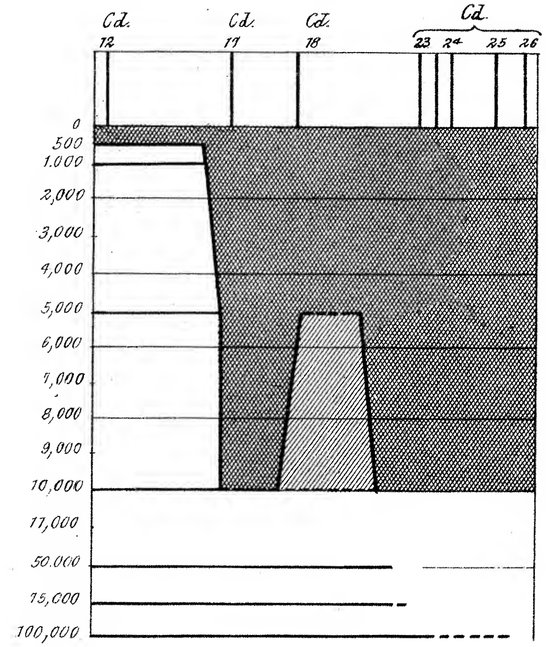


Ordinates = the proportion of water to 1 part by weight of Thymol.

Thickness of layer of liquid = 0·75 inch.

No. 12.

Pyrogallol. $C_6H_3(OH)_3$.



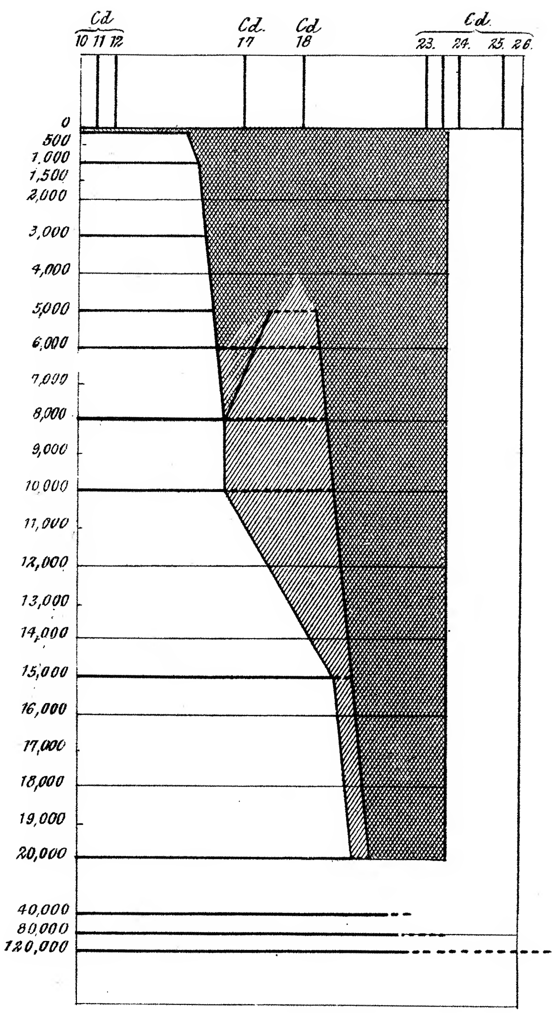
Ordinates = the proportion of solution containing 1 part by weight of substance.

Thickness of layer of liquid = 0·75 inch or 19 m.

Harrison & Sons, Lith. St. Martins Lane, W.C.

N° 13.

Benzoic Acid. C_6H_5COOH.

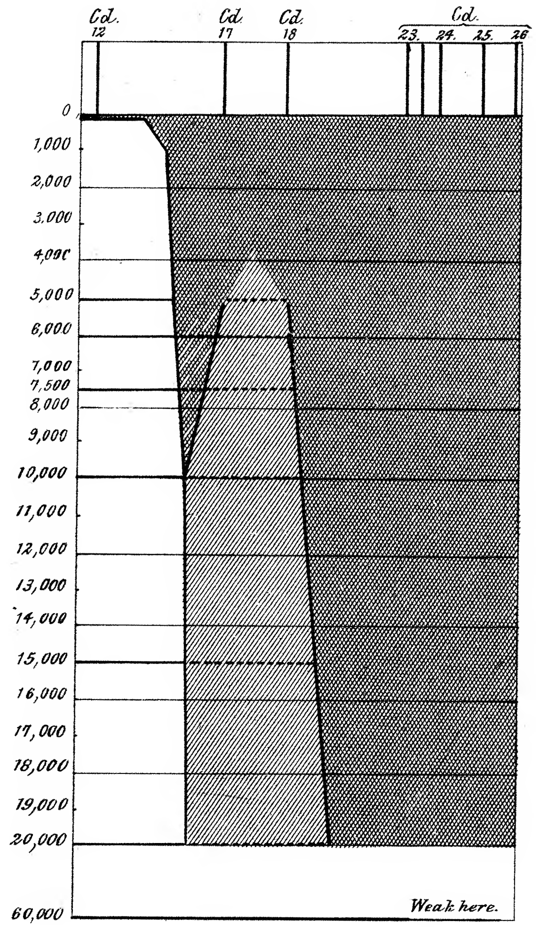


Ordinates = the proportion of water to 1 part by weight of Benzoic Acid.

Thickness of layer of liquid = 0.75 inch.

N° 14.

Phthalic Acid. $C_6H_4(COOH)_2$



Absorption occurs at the more refrangible part of the spectrum in solutions containing 300,000 parts of water.

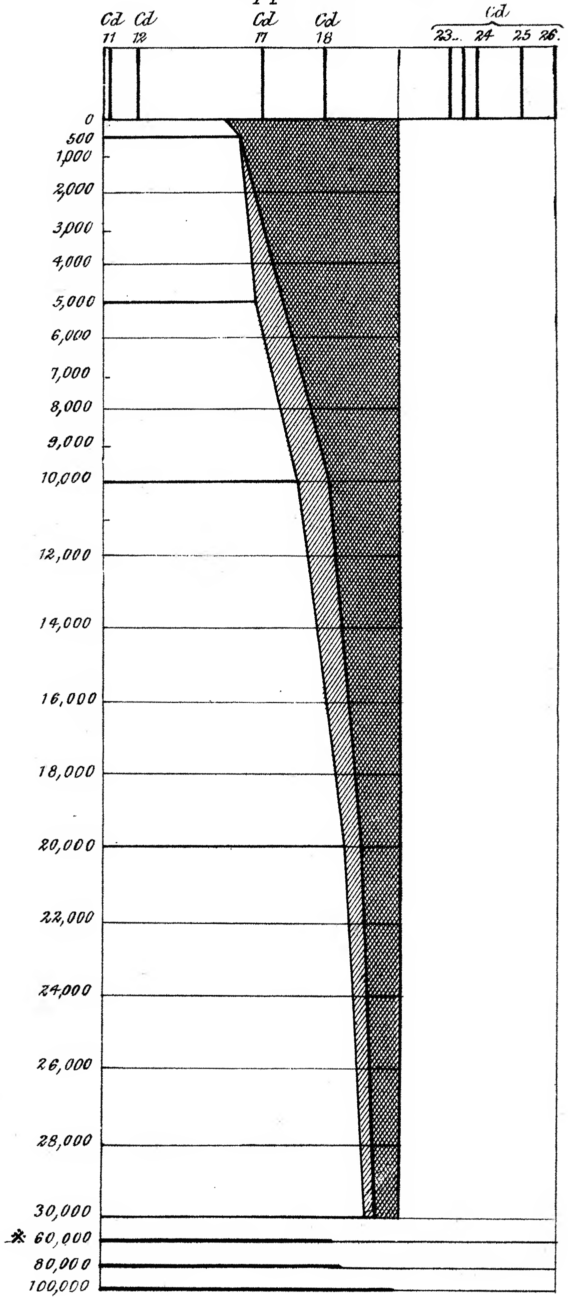
Ordinates = the proportion of water to 1 part by weight of Phthalic Acid.

Thickness of layer of liquid = 0.75 inch.

Three times the exposure does not effect any alteration in the spectrum.

N° 15.

Hippuric Acid.



Ordinates = The proportion of Hippuric Acid to 1 part by weight of water.

Thickness of layer of liquid = 0.75 inch.

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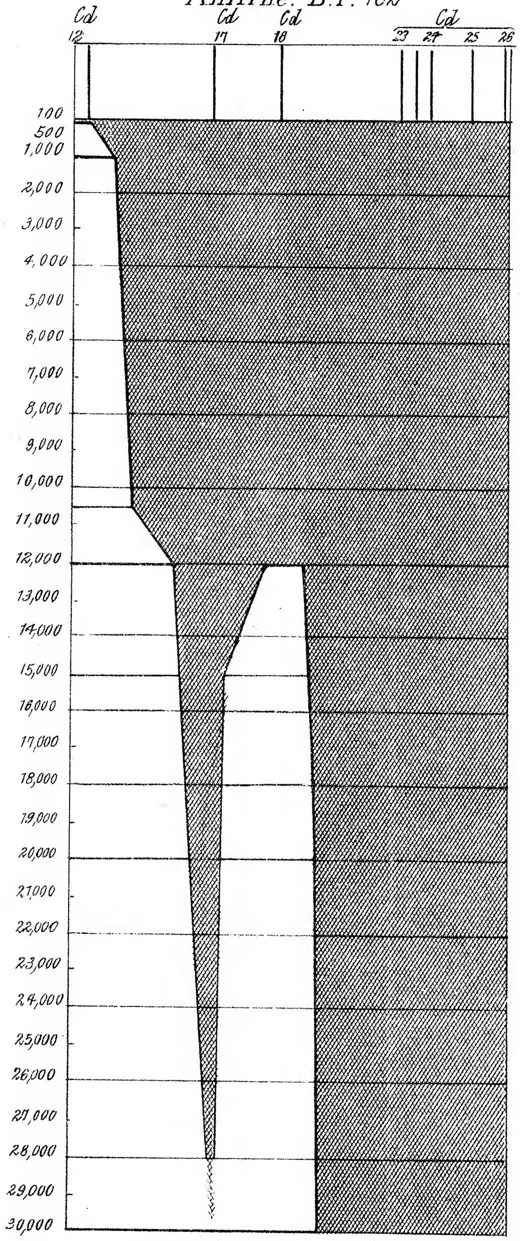
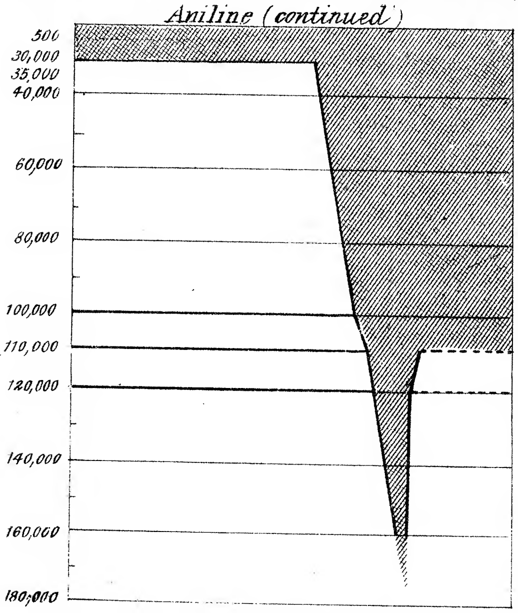
Nº 16.

Aniline. B.P. 182°



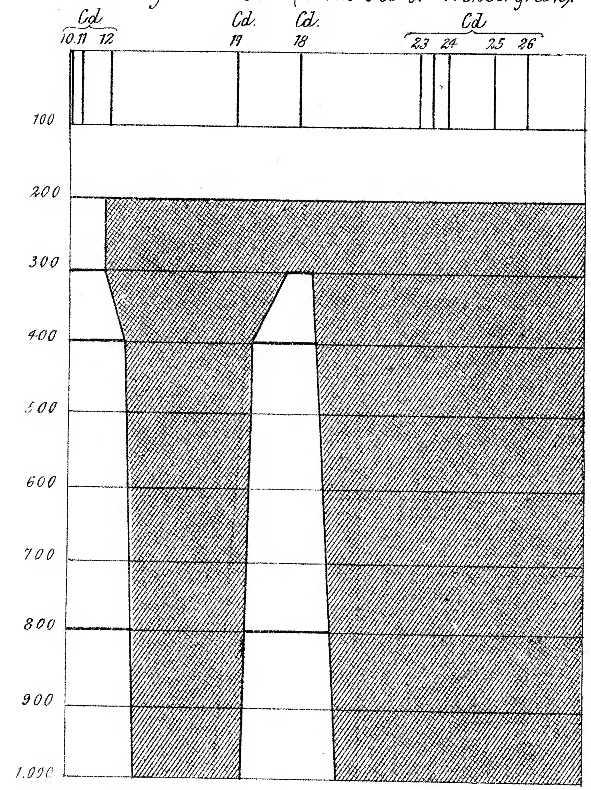
Aniline (continued)



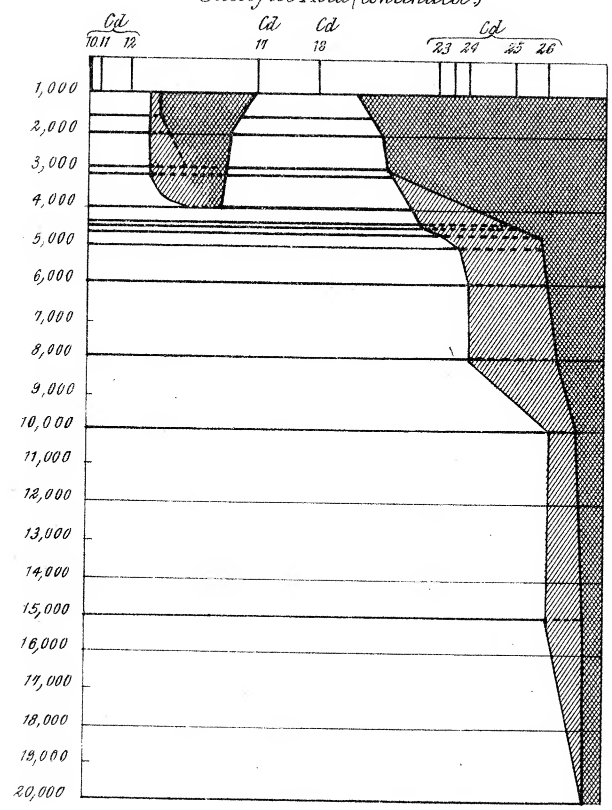
The Aniline was first diluted with Alcohol and then with water.

Nº 17.

Salicylic Acid (from Oil of Wintergreen).



Salicylic Acid (continued.)



Ordinates = the proportion of water to 1 part by weight of Salicylic Acid.

Thickness of layer of liquid = 0.75 inch.

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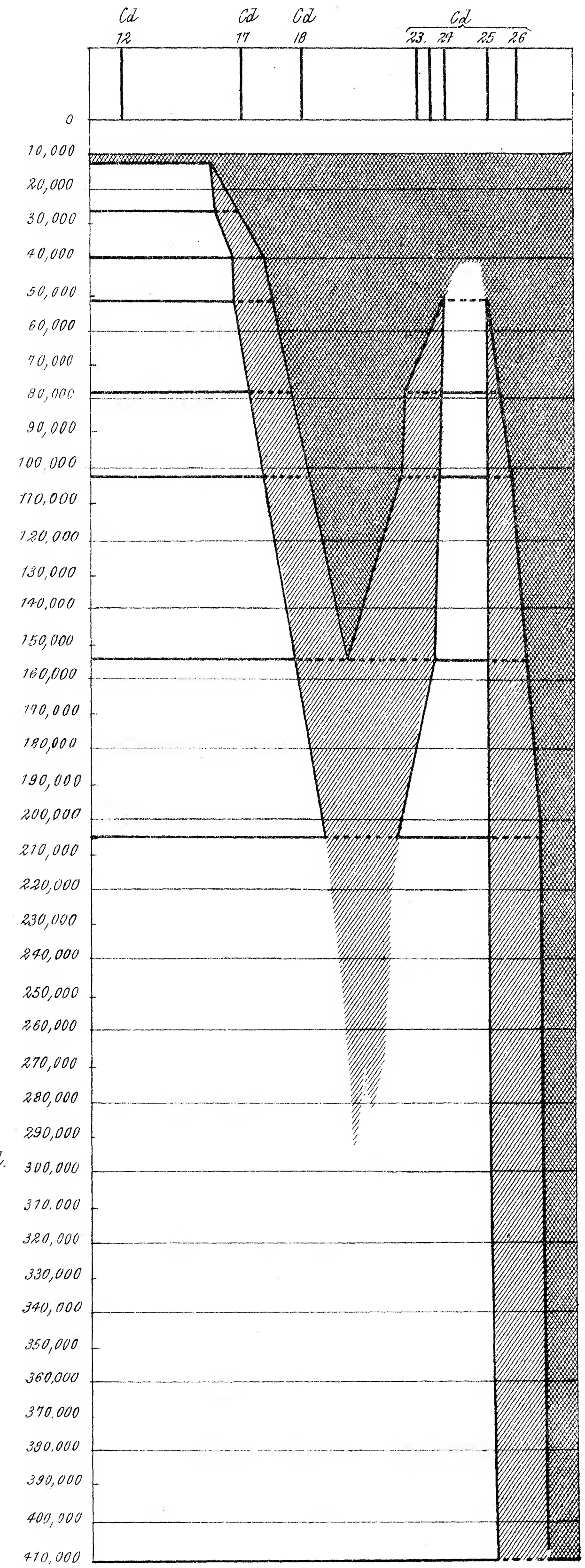
N° 19.

Paroxybenzoic Acid.

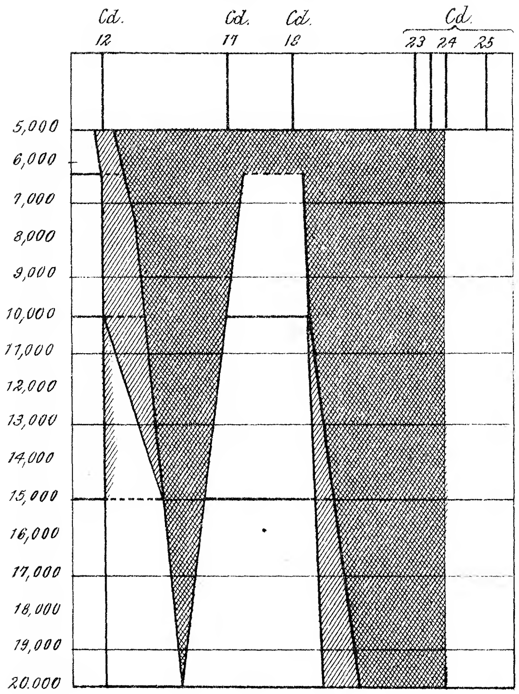


Ordinates = The proportion of water to 1 part by weight of Paroxybenzoic Acid.

Thickness of layer of liquid = 0.75 inch.

N° 18.

Oxybenzoic Acid (1.3)



Ordinates = The proportion of water to 1 part by weight of Oxybenzoic Acid.

Thickness of layer of liquid = 0.75 inch.

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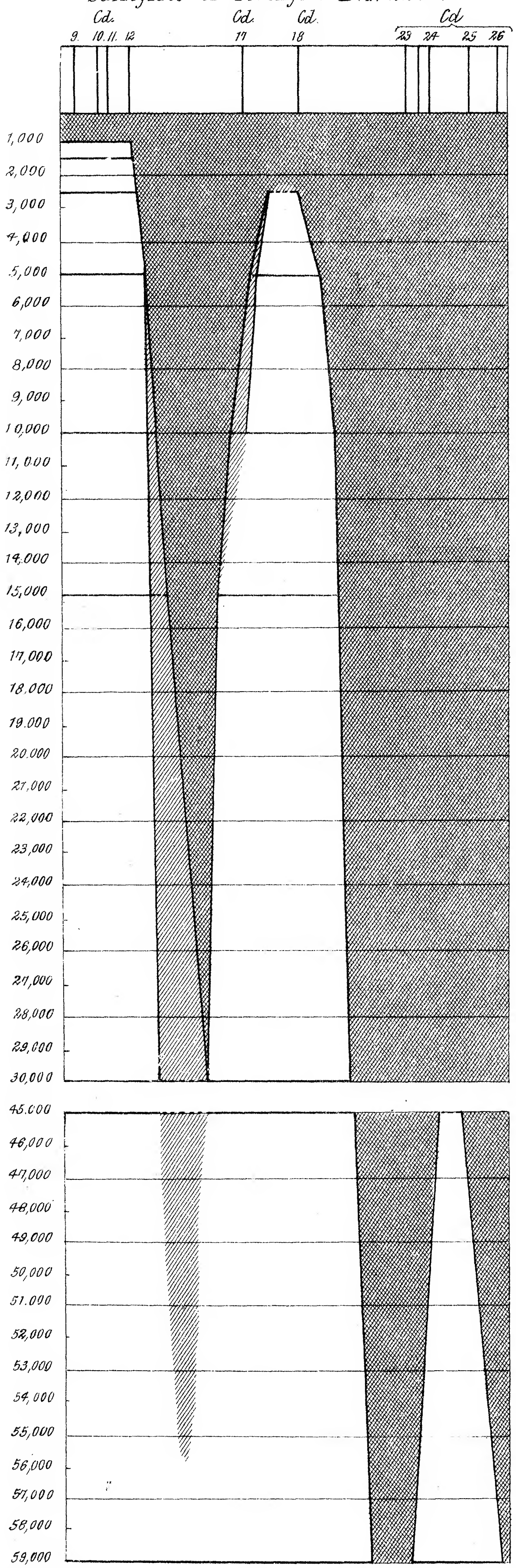
Nº 20.

Salicylate of Methyl — B.P. 220°·7

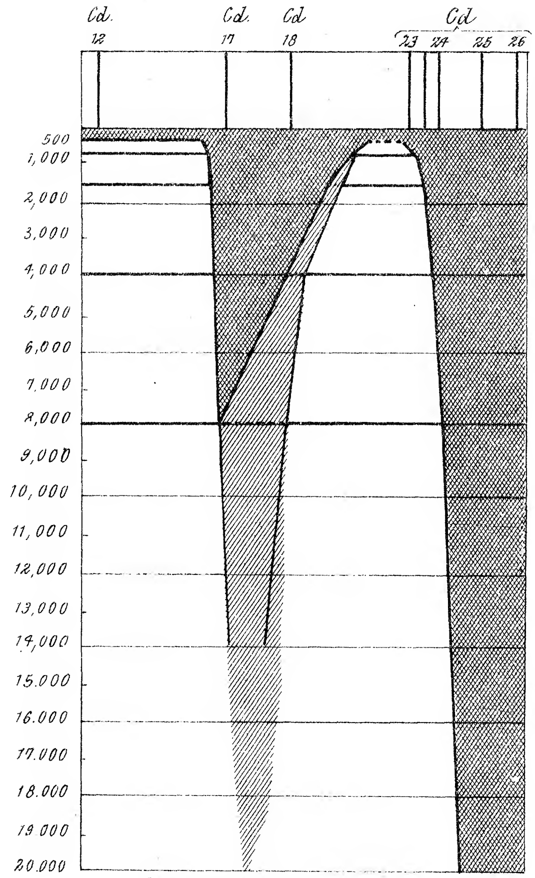


Ordinates = the proportion of diluent to 1 part by weight of the substance.

Thickness of layer of liquid = 0.75 inch.

Nº 21.

Salicine. $\left.\begin{matrix} C_6 H_{11} O_5 \\ C_6 H_4(OH) CH_2 \end{matrix}\right\} O$



The absorption band is traceable in solutions containing $\frac{1}{50,000}$ of the substance.

Thickness of layer of liquid = 0.75 inch.

Ordinates = the proportion of solution containing one part by weight of the solid substance.

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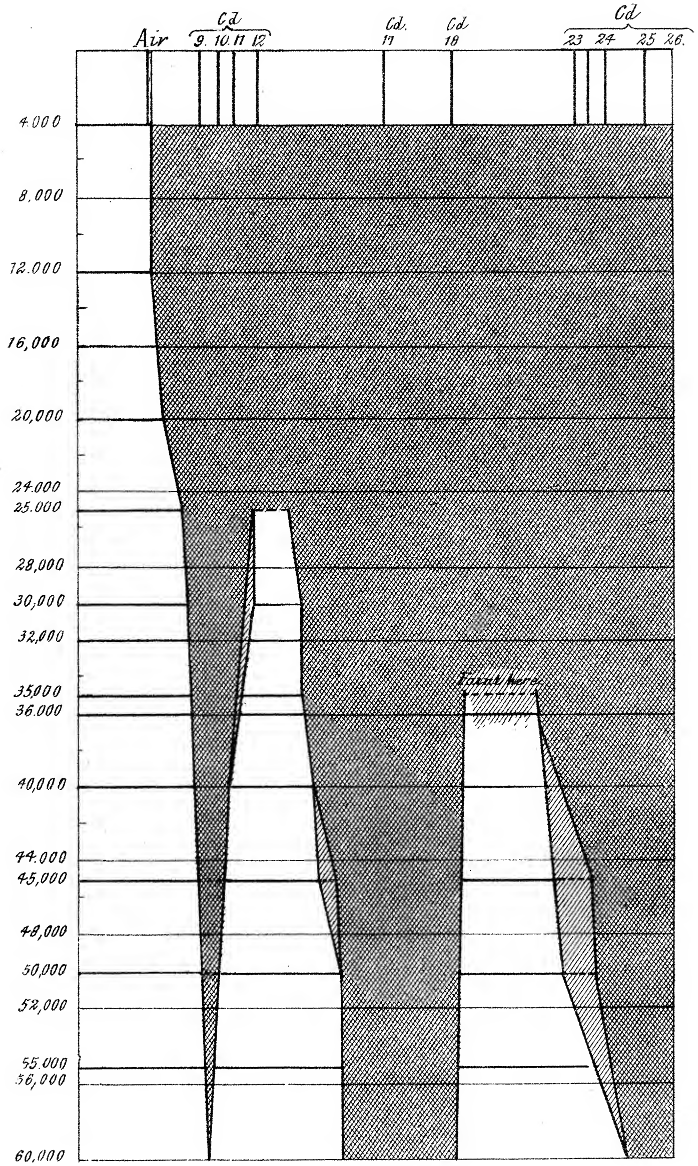
No. 22.

Orthonitro-phenol.



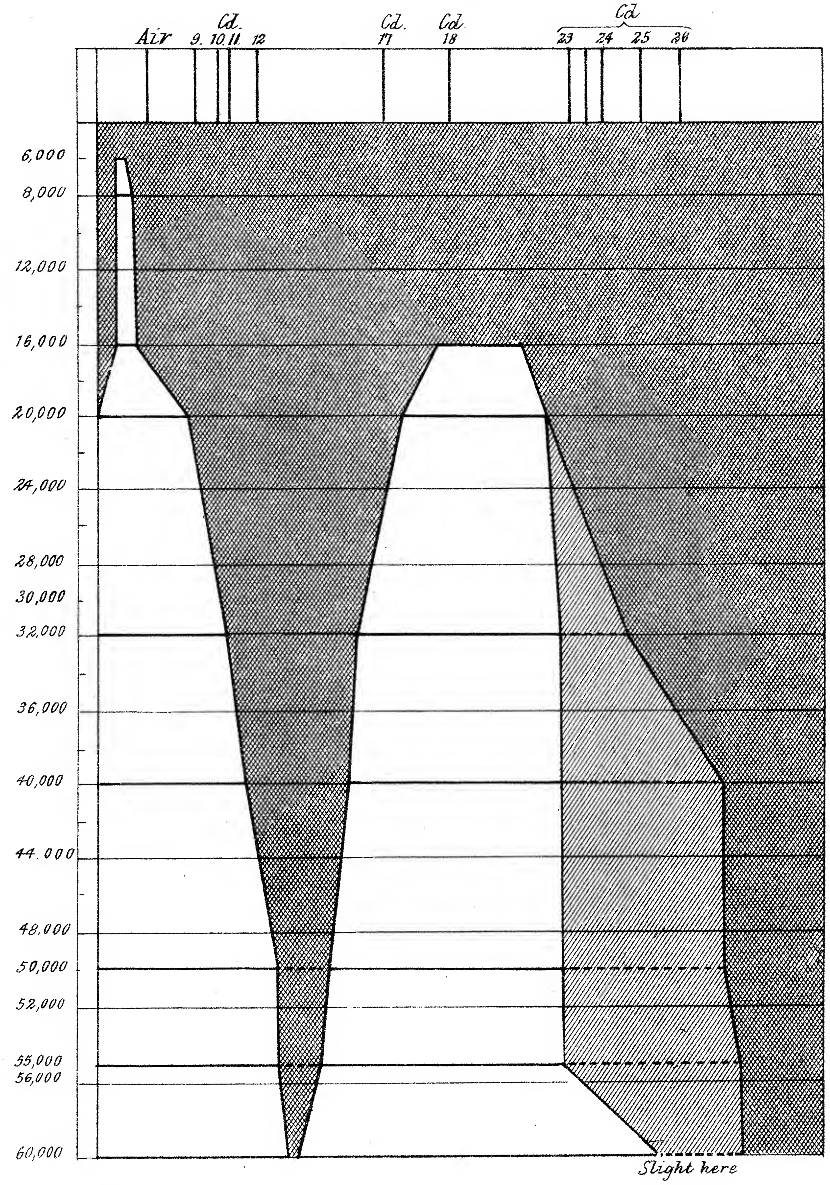
The spectrum can be traced across, but is weak just here and is not free from absorption at $\frac{1}{120,000}$.

Ordinates = the proportion of water to 1 part by weight of Orthonitrophenol.

Thickness of layer of liquid = 0.75 inch.

No. 23.

Paranitro-phenol.



Ordinates = the proportion of water to 1 part by weight of Paranitrophenol.

Thickness of layer of liquid = 0.75 inch.

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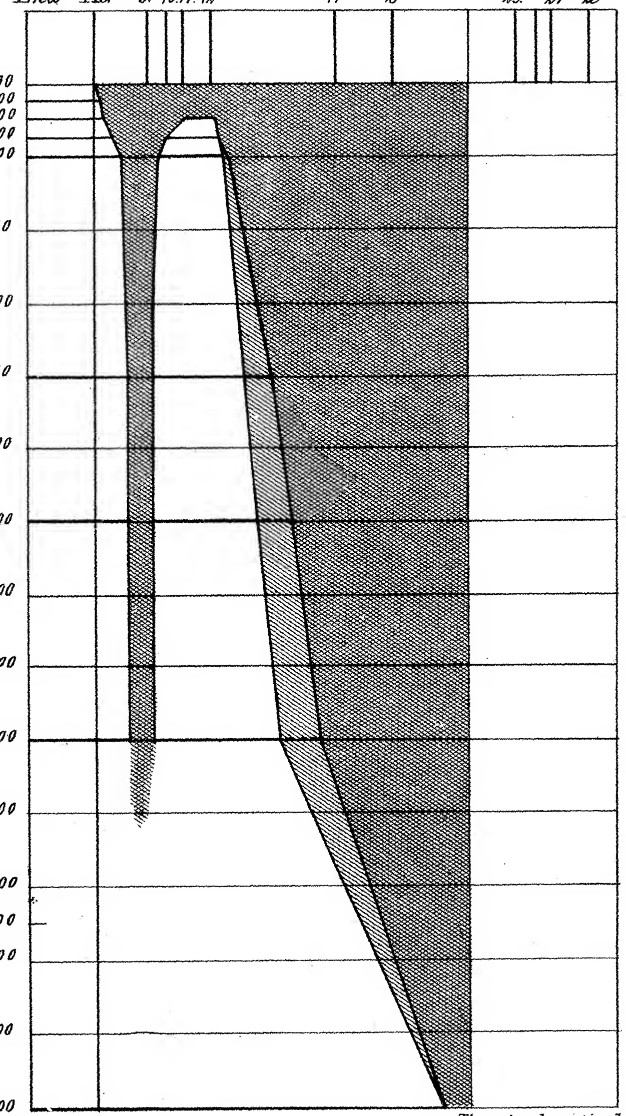
No. 24.

Meta-nitraniline. 1·3.



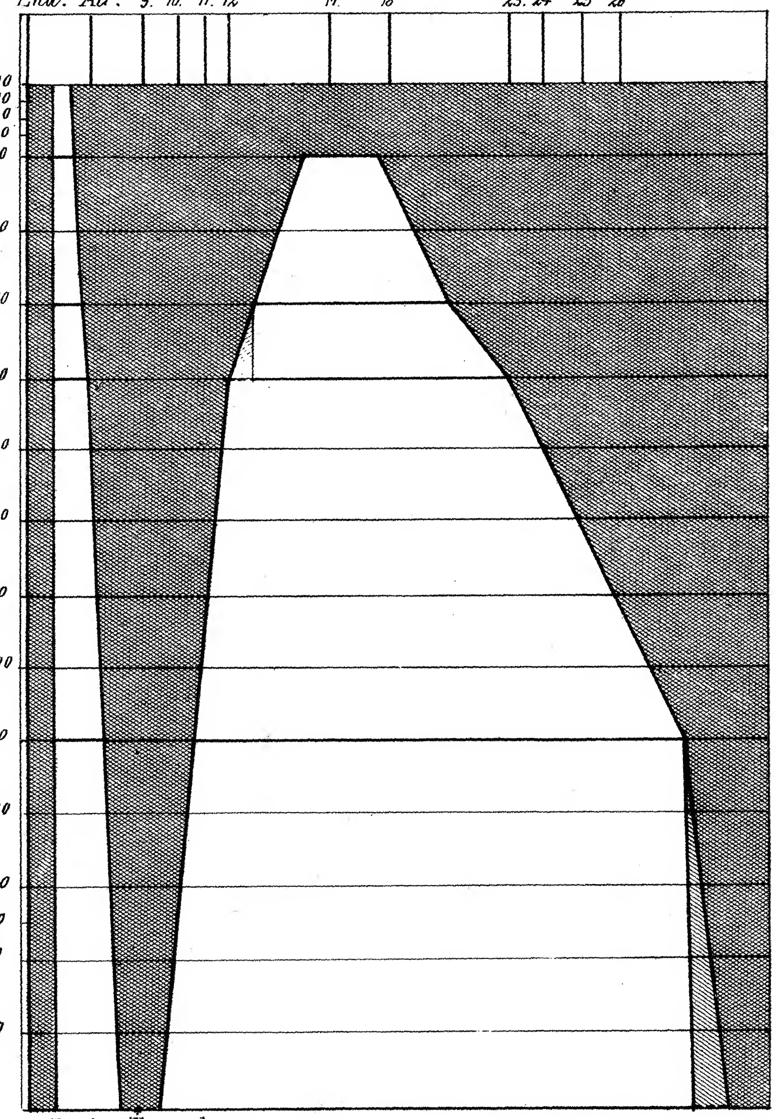
There is absorption here up to 120,000.

Ordinates = the proportion of water to 1 part by weight of Metanitraniline.

Thickness of layer of liquid = 0.75 inch.

No. 25.

Para-nitraniline. 1·4.



There is still a weakness up to 100,000 at this point.

Ordinates = the proportion of water to 1 part by weight of Paranitraniline.

Thickness of layer of liquid = 0.75 inch.

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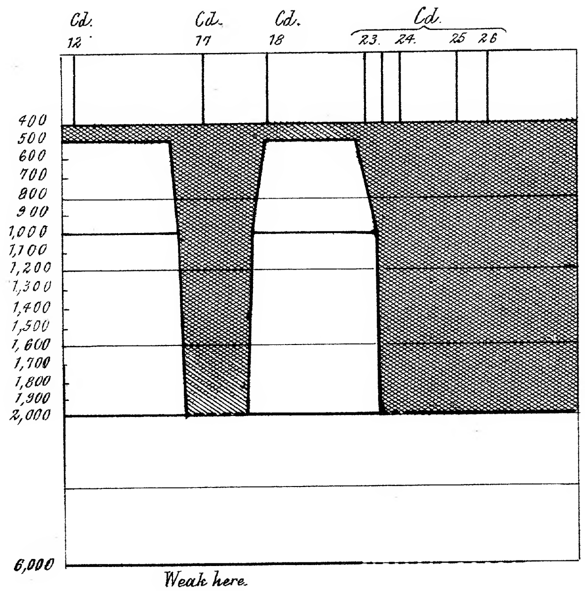
No. 26.

Tyrosine.

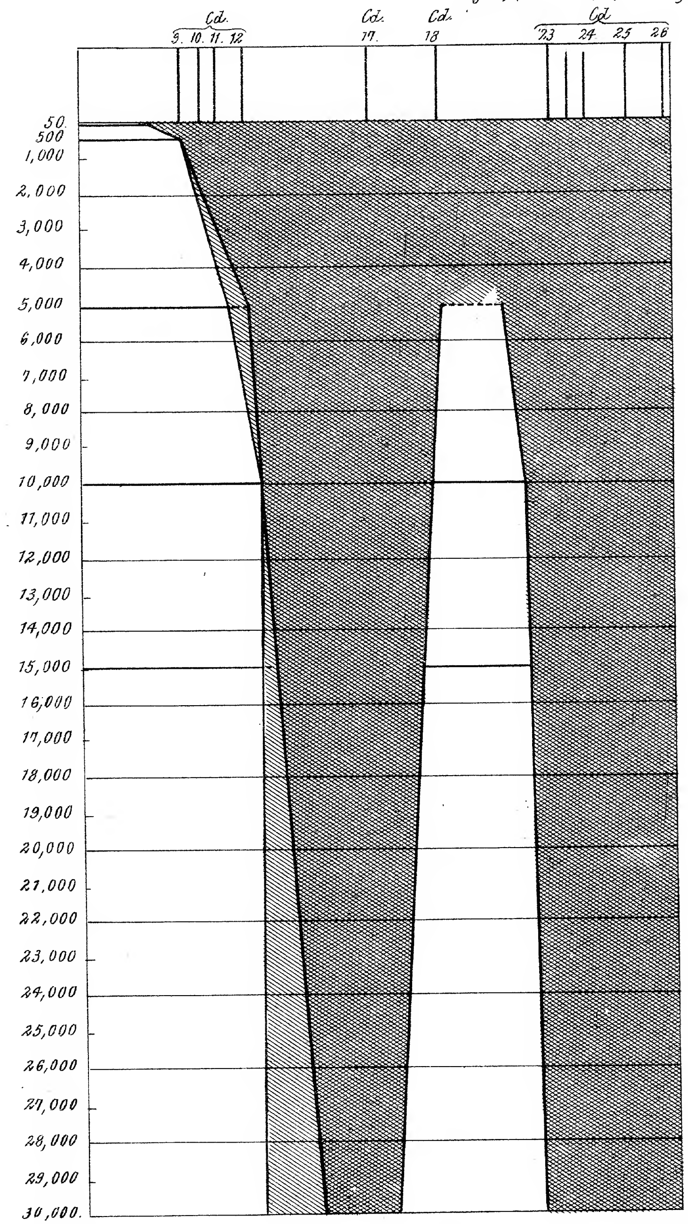


Ordinate = the proportion of water to 1 part by weight of Tyrosine.

Thickness of layer of liquid = 0.75 inch.

No. 27.

Phlorizine. – *Structural formula* = $\left.\begin{array}{l}\left.\begin{array}{r}C_6 \cdot H_{11} \cdot O_5 . \\ C_6 \cdot H_3\,(OH)\end{array}\right\} O. \\ C_6H_4\,(OH)\,C_2H_4 \cdot CO\end{array}\right\} O.$



There is very perceptible absorption here in solutions containing only $\frac{1}{50,000}$ of Phlorizine.

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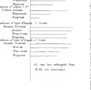
No 3

Diagram showing the absorption of the ultra violet rays by sodium and barium salts of the Fatty Acids in molecular proportions



All rays less refrangible than 12 Cd. are transmitted.